DISINFECTION BYPRODUCTS IN DESALINATED AND BLENDED WATER: HUMAN EXPOSURE AND RISK ANALYSIS

BY

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This thesis is dedicated to my family

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LIST OF ABBREVIATIONS

BCAA	:	Bromochloroacetic Acid
BCAN	:	Bromochloroacetonitrile
BCM	:	Billion Cubic Meter
BDCAA	:	Bromodichloroacetic Acid
BDCM	:	Bromodichloromethane
CAN	:	Chloroacetonitrile
CDI	:	Chronic Daily Intake
CH	:	Chloral Hydrate
DALY	:	Disability Adjusted Life Year
DBAA	:	Dibromoacetic Acid
DBAN	:	Dibromoacetonitrile
DBCAA	:	Dibromochloroacetic Acid
DBCM	:	Dibromochloromethane
DBP	:	Disinfection Byproduct
DCAA	:	Dichloroacetic Acid
DCAN	:	Dichloroacetonitrile

DCP	:	1,1-dichloropropanone
DOC	:	Dissolved Organic Carbon
DW	:	Desalinated Water
GW	:	Groundwater
HAA	:	Haloacetic Acid
HAN	:	Haloacetonitrile
HK	:	Haloketone
MBAA	:	Monobromoacetic Acid
MC	:	Monte Carlo
MCAA	:	Monochloroacetic Acid
MCM	:	Million Cubic Meter
MED	:	Multiple Effect Distillation
MOEP	:	Ministry of Economy and Planning
MOWE	:	Ministry of Water and Electricity
MSF	:	Multistage Flash Distillation
MTBE	:	Methyl Tertiary Butyl Ether
MX	:	3–chloro–4-(dichloromethyl)-5–hydroxyl-2(5H)-furanone

NDEA	:	N-nitrosodiethylamine
NDMA	:	N-nitrosodimethylamine
NOM	:	Natural Organic Matter
OSW	:	Office of Saline Water
PPPY	:	Per Person Per Year
R_fD	:	Reference Dose
RO	:	Reverse Osmosis
SF	:	Slope Factor
SW	:	Surface Water
SWCC	:	Saline Water Conversion Corporation
TBAA	:	Tribromoacetic Acid
TCAA	:	Trichloroacetic Acid
TCAN	:	Trichloroacetonitrile
TCP	:	1,1,1-trichloropropanone
THFMP	:	Trihalomethane Formation Potential
THM	:	Trihalomethane
TIC	:	Total Ion Count

TOC	:	Total Organic Carbon
TTHM	:	Total Trihalomethanes
TWW	:	Treated Wastewater
USEPA	:	United States Environmental Protection Agency
VC	:	Vapor Compression
YLD	:	Years of Life Lost Due to Disability
YLL	:	Years of Life Lost

ABSTRACT

Full Name : [MD. IMRAN RAHMAN CHOWDHURY]

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[Desalinated seawater satisfies significant fractions of domestic water demands in many countries. The desalinated seawater and/or blended water contains various types of disinfection byproducts (DBPs), some of which may induce cancer risks to human through lifetime exposure. In this study, occurrences of trihalomethanes (THMs) in desalinated and blended water in Saudi Arabia, the largest producer of desalinated water, were investigated and their exposure and risks were predicted. The chronic daily intakes of $CHCl_3$, BDCM, DBCM, and $CHBr_3$ were estimated to be 8.38×10^{-5}, 7.57×10^{-5}, 2.54×10^{-5} and 4.32×10^{-4} mg/kg-day respectively. The overall cancer risk was 1.78×10^{-5} with the range of 7.40×10^{-7} – 9.26×10^{-5} and the average hazard index was 3.49×10^{-2} with the range of 1.20×10^{-3} – 2.34×10^{-1}. There are 100, 77.5, 1.2 percent chances that cancer risks can exceed the risk levels of 1×10^{-6}, 1×10^{-5} and 5.0×10^{-5} respectively. The loss of disability adjusted life years (DALY) were estimated to be 25.1 per year and the average cancer risk had 8.48×10^{-7} DALY per person per year. The financial burden was estimated to be US$2.72 million with the range of US$2.52–2.91 million. The findings may assist in better understanding and reducing cancer risks from DBPs in desalinated and blended water.]

ملخص الرسالة

الاسم الكامل: مد. عمران رحمن شودهارى

عنوان الرسالة: المنتجات الثانويه الناتجه عن تعقيم المياه المحلاه و المخلوطه: التعرض البشري و تحليل المخاطر

التخصص: الهندسة المدنية والبيئية

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تلبي مياه البحر المحلاة احتياجات كبيرة من الطلب على المياه المحلية في العديد من الدول. كما تحوي مياه البحر المحلاة و/أو المياه المخلوطة أنواعاً مختلفة من مخلفات التطهير (Disinfection Byproducts)، والتي قد تعزز بدورها من مخاطر الإصابة بالسرطان. إن هذه الدراسة تقوم بفحص تركيز مادة ثلاثي الهالوميثان (Trihalomethanes) في المياه المحلاة والمخلوطة في المملكة العربية السعودية والتي تعدّ من أكبر منتجي المياه المحلاة، بالإضافة الى التنبؤ بالمخاطر المحتمل حدوثها لتواجد مثل هذه المادة في المياه. تم تقدير المدخول اليومي للتعرض المزمن للمواد التالية $CHCl_3$، BDCM، DBCM و$CHBr_3$ لتكون 8.38×10^{-5}، 7.57×10^{-5}، 2.54×10^{-5} و 4.32×10^{-4} ملغ / كغ يومياً على التوالي. وكان المقدار الكلي لخطر الاصابة بالسرطان ما يقارب 1.78×10^{-5} ويتراوح من 40.7×10^{-7} الى 9.26×10^{-5} كما أن متوسط مؤشر الخطر وصل إلى ما يقارب 3.49×10^{-2} ويتراوح من 1.20×10^{-3} الى 2.34×10^{-1}. إن النسب التالية: 100، 77.5، 1.2 في المئة تمثّل احتمالات مخاطر الإصابة بالسرطان والتي يمكن أن تتجاوز مستويات مؤشر الخطر بما يقارب 1×10^{-6}، 1×10^{-5} و 5.0×10^{-5} على التوالي. تم تقدير خسائر الإعاقة لتعديل سنوات العمر المعروفة بـ (DALY) بما يقارب 25.1 سنويا. وقد كان متوسط خطر الإصابة بالسرطان ما يقارب 8.48×10^{-7} DALY للشخص الواحد سنوياً. تم تقدير الاعباء المالية بما يقارب 2.72 مليون دولار ويتراوح ما بين 2.52 – 2.91 مليون دولار أمريكي. هذه النتائج يمكن أن تسهم في فهم أفضل لمخاطر الإصابة بالسرطان بالإضافة إلى تقليل المخاطر الناتجة عن مخلفات التطهير في المياه المحلاة والمخلوطة.

CHAPTER 1

INTRODUCTION

Saudi Arabia is a semi-arid country with low annual rainfall. Out of the total area of approximately 2.15 million square kilometers [1], about 90% of the country is covered with deserts and plain lands [2]. The current population is approximately 31.6 million [3], which is growing at the rate of 2.6% per year [4]. In 2009, total water demand in the country was 18500 million cubic meters (MCM), in which 84% was used for agriculture. The total water demand was reduced to 16300 MCM in 2014, due mainly to the reduction of agricultural water demand [5,6]. During this period, industrial and domestic water demands were increased by 5.5% and 2.1% per year [5,6].

Water scarcity is a critical issue in Saudi Arabia. The domestic water demand was approximately 2583 MCM per year [7,8]. The total supply of desalinated water (DW) in 2014 was reported to be approximately 1600 MCM [4], indicating that more than 60% of domestic water demands are satisfied by the desalinated water [7,9]. The desalinated water is blended with treated groundwater, disinfected with chlorine, pH adjusted and transported through the distribution networks to the consumers. In the coming years, contributions of desalinated water are likely to be increased [7]. In Saudi Arabia, desalinated water is produced by desalinating the seawater from the Arabian Gulf and the Red Sea in the east and west, respectively, of the country. In the Arabian Gulf, average concentration of bromide was 64,000 µg/L [10]. The World Health Organization reported concentrations of

iodide and bromide in the ranges of <1 – 30 µg/L and 50,000 – >80,000 µg/L respectively [11,12]. According to past studies, concentrations of iodide and bromide were varying between the ranges of 21 – 60 µg/L and 50,000 – 80,000 µg/L, respectively [10,13–20]. Although most of the iodide and bromide (>99%) were removed during desalination, concentrations of iodide and bromide were reported to be <4 – 16 µg/L and 250 – 600 µg/L, respectively [13,14,18,20,21]. Because of the saline water intrusion, the groundwater aquifers in the coasts might have been polluted. It might be one of the causes of higher levels of bromide in groundwater in the Arabian region [22].

To supply domestic water, desalinated water is blended with treated groundwater, pH adjusted and chlorinated to prevent microbiological contamination in the water distribution network. Generally, desalinated water contains lower levels of natural organic matter (NOM) and higher levels of bromide while the treated groundwater contains relatively higher levels of NOM [23–25]. Consequently, the blended water contains higher levels of bromide and NOM, which can produce many types of disinfection byproducts (DBPs) upon chlorination. Further, DBPs in the treated groundwater, which are formed during treatment using chlorine, are also added to the blended water. In addition, DBPs can also be formed during pretreatment for seawater, which is also added to the blended water [20]. To date, over 100 types of DBPs have been reported in drinking water. The most investigated DBPs include trihalomethanes (THMs), haloacetic acids (HAAs), halonitriles, haloketones (HKs), haloaldehydes, chloral hydrates (CH), haloacetonitriles (HANs), halo- and nitro phenols, halodiacids, bromate, haloamides, aromatic halogenated DBPs, haloacids, haloalcohols, nitrosamines (e.g., *N*-nitrosodimethylamine [NDMA]), iodo-THMs, 3–chloro–4–(dichloromethyl)–5–hydroxyl–2(5H)–furanone (MX) and MX homologues, and

halonitromethanes [26–29] etc. The existence of bromide elevates the percentages of brominated DBPs in blended water, while the brominated DBPs are more toxic and many of these DBPs are probable or possible human carcinogen [30]. Few of these DBPs might be related to human cancer and other chronic and sub-chronic effects of human health [26,27,31–36]. The populations are possibly exposed to these DBPs through ingestion of drinking water, inhalation, dermal absorption during regular activities (e.g., showering, bathing, cooking, house cleaning), and swimming in a chlorinated/brominated swimming pools [37–40]. Although many studies have focused on the exposure and risks from DBPs in ground or surface water sourced drinking water, limited information is available on exposure and risks from DBPs in desalinated and/or blended water. There is a necessity of enhanced understanding of the exposure and risks from DBPs in desalinated and blended water in Saudi Arabia.

1.1 A Brief History of Desalination

The first inscribed portrayal of desalination is available in the Old Testament, in Exodus about 1500 BC [41,42]. Philosophical ideas about desalination were first expressed by the Greeks in 640 – 546 BC [43,44]. The famous philosopher, Aristotle described the source and characteristics of natural, brackish and seawater [45,46]. A Greek alchemist, Cleopatra the Wise [42,47] developed distillers in the Hellenistic period. In the 7th century, the Arabs termed the distillers as Al-Ambiq. In 1589, Giovani Batista Della Porta mentioned seven processes of desalination, in which solar distillation process along with the apparatus was described to convert brackish water into fresh water [42,48,49]. Wheeler and Evans were granted the first American patent on solar distillation in 1870. The foremost large scale

solar distillation plant was designed and built in 1872 by Carlos Wilson, a Swedish engineer. There were only a few solar distillation plants till the Second World War. Many small plastic solar distillation equipment and machineries were built for the US Navy during the War [50]. The Office of Saline Water (OSW) was established by the US Secretary of the Interior in July 1952. OSW promoted desalination applications through research and development. The research and developments were marked through the publications of research and progress reports. The organization constructed five demonstration plants. In Daytona Beach, OSW established an experimental station [51]. In the Caribbean Islands, under the supervision of McGill University in Canada, several small-scale solar distillation plants were established in the following years. In New Delhi, India, experimental works were performed on solar distillation under the supervision of the National Physical Laboratory. The information about all solar distillation plants and solar stills experimented or/and constructed up to 1970, was reported by the Battelle Memorial Institute at Columbus, OH [51]. In context to Saudi Arabia, the first desalination plant was established in 1980 and the initial production of desalinated water was approximately 7.7 million cubic meter (MCM) [9]. As of today, the country produces approximately 1600 MCM of desalinated water annually, which has made the country as the largest producer of desalinated water as a single country [5]. The desalinated water is mostly applied for domestic activities in the major regions, including Riyadh, Makkah, Madinah, Qaseem, Eastern Region, Aseer, Jeddah, Tabouk and Jazan [52].

1.2 Study Area

The Kingdom of Saudi Arabia is situated in the arid region within latitude: 16.5ºN – 32.5ºN and longitude: 33.75ºE–56.25ºE, which has an area of about 2.3 million square kilometers, surrounded by the Red Sea in the west, the Arabian Gulf in the east and near the Arabian Sea in the south [53]. The West highlands rise up to 3,000 meters along the Red Sea and the land down gently towards the east [53]. There are thirteen administrative regions in the Kingdom: Riyadh, Makkah, Madinah, Qaseem, Eastern region, Aseer, Hail, Tabouk, Al-Baha, Northern borders, Al-Jouf, Jazan, and Najran [4]. Among these regions, Riyadh, Makkah, Madinah, Qaseem, Eastern Region, Aseer, Tabouk and Jazan receive desalinated water to partially satisfy the domestic water demands while the other regions satisfy the domestic water demands using the groundwater sources and/or storage reservoirs [8]. The study area of this study is shown in Figure 1.1 [54]. The colored areas within Saudi Arabia indicate the regions, which receive desalinated water.

Figure 1.1: Location of regions receiving desalinated water [54]

The climate of the country is semi-arid, typically described by cold and slightly wet winter with hot and dry summer [53]. The long-term mean annual rainfall is about 100 mm [4], which varies from 70.1 mm/year in the northern part to 264.6 mm/year in the southern part of the country [4]. Water resources (groundwater and surface water) are limited in the country. There is no natural surface water flow in the entire country. There are 449 dams, mostly located in the south and southwestern regions of Saudi Arabia. These dams have the storage capacity of approximately 2000 MCM of seasonal rainfall [5,7]. In 2013, the total desalinated water produced in the country was approximately 1600 MCM, in which the Saline Water Conversion Corporation (SWCC) operated 28 plants produced approximately 1019.5 MCM and the private organization produced approximately 575.5 MCM respectively [5]. The highest amount of desalinated water was produced in Al-Jubail desalinated plant (368 MCM) followed by Al-Shoaibah Third Stage plant (278 MCM), Al-Shoaibah desalinated plant (165 MCM), Jubail Facilities (163.5 MCM). The production of desalinated water by the SWCC operated plants and private sectors are presented in Tables 1.1 and 1.2 respectively.

Table 1.1: The amounts of desalinated water exported from the general organization for desalination plants in 2013 [5]

Plant	Quantity (MCM)
Jubail (3 Plants)	368
Al-Shoaibah (2 Plants)	165
Al-Khobar (2 Plants)	130
Jeddah (4 Plants)	160
Yanbu (4 Plants)	137
Al-Shaqaiq	28.5
Al-Khafji	7.5
The small plants (10 Plants)	23.5
Total	1019.5

Table 1.2: Desalinated water exported from the private desalination plants in 2013 [5]

Plant	Quantity (MCM)
Al-Shoaibah (third stage)	278
Jubail Facilities	163.5
Al-Shaqaiq	66.5
Al-Shaqaiq Expansion (RO)	53.5
Al-Bawarij	14
Total	575.5

The approximate locations of the desalination plants near the Red Sea and the Arabian Gulf are shown in Figures 1.2 and 1.3 respectively. The Figures include all plants that are supplying desalinated water or in under-construction. The locations of all plants with capacities >1000 m^3/day are shown on the map. In addition, desalination plants with capacities more than 100,000 m^3/day are identified specifically. The total capacity and the designed capacity of each plant is stated in the Figures 1.2 and 1.3.

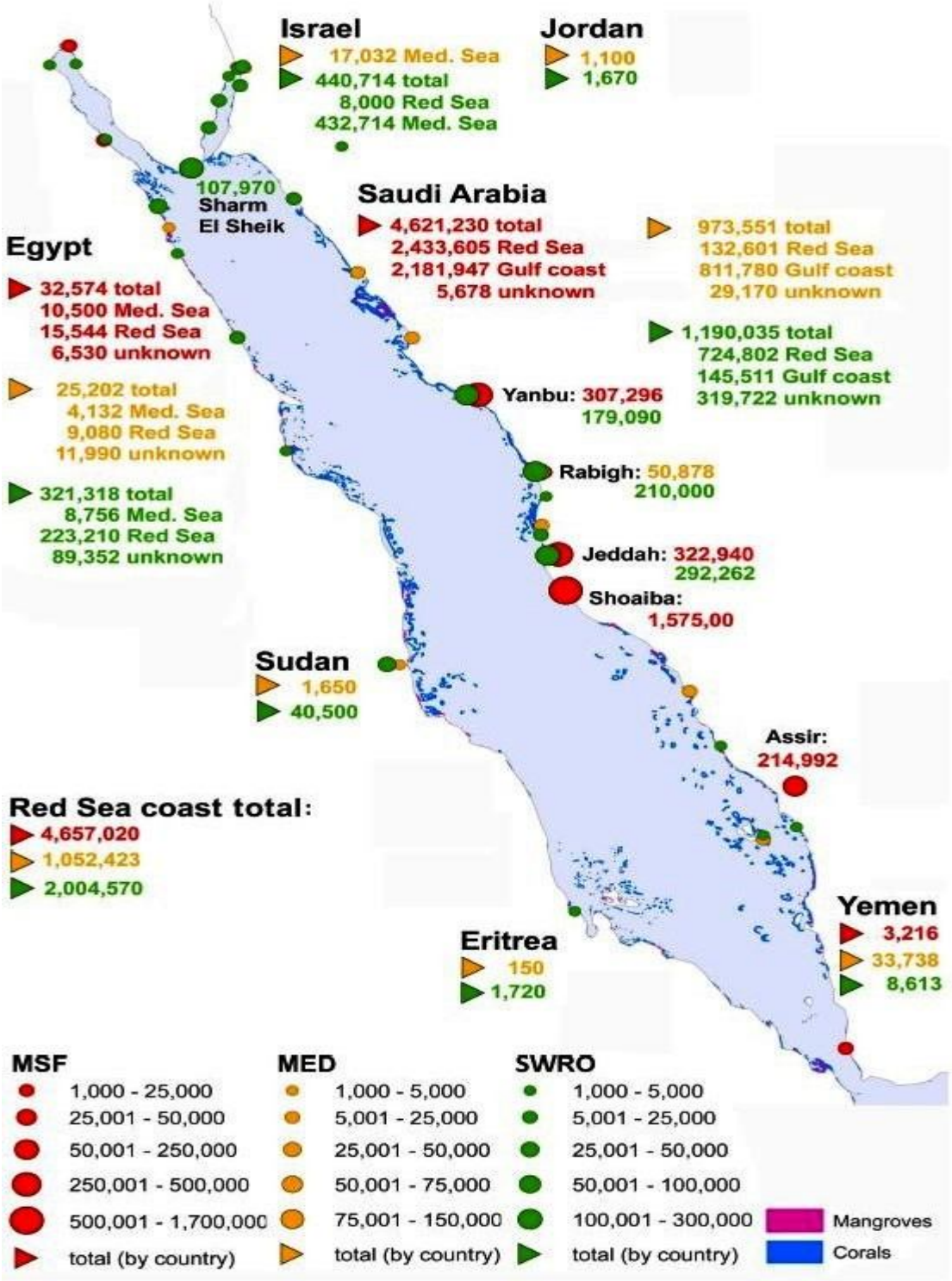


Figure 1.2: Locations of desalination plant near the Red Sea [55]

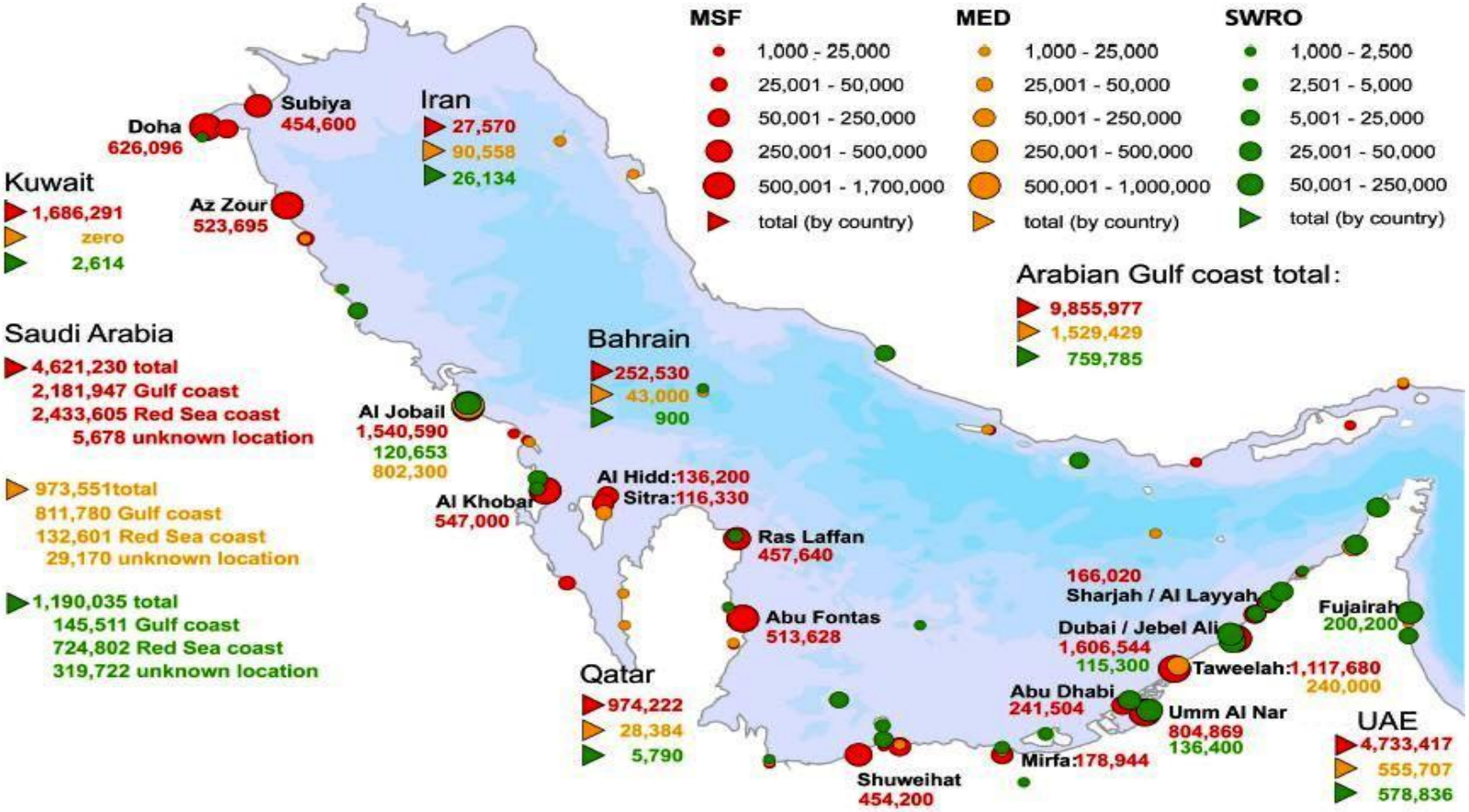


Figure 1.3: Locations of desalinated plants near the Arabian Gulf [55]

1.3 Summary of Contribution

This study estimated human exposure and risk from DBPs in desalinated seawater and blended water in Saudi Arabia. The goal is achieved through achieving the following objectives:

i. Characterizing the occurrences of trihalomethanes (THMs) in desalinated seawater and blended water from different desalination plants in Saudi Arabia.
ii. Characterizing different exposure scenarios for THMs in desalinated seawater and blended water via ingestion, inhalation and dermal absorption.
iii. Predicting cancer and non-cancer risks from exposure to THMs in Saudi Arabia through multiple exposure pathways following probabilistic approach.
iv. Estimating the disability adjusted life year (DALY) using the concept of YLL (years of life lost due to premature death) and YLD (years of life lost due to disability) due to the exposure to THMs.
v. Predicting the financial burdens from such losses.
vi. Highlight the exposure, risk control strategies and future research directions.

1.4 Organization of Thesis

This thesis work is divided into seven chapters. The introduction of the thesis is presented in Chapter 1.

Chapter 2 describes the background of this thesis. It includes water resources in Saudi Arabia, theory of disinfection byproduct formation and chemistry of disinfectants. The necessity of exposure and risk analysis was described.

In Chapter 3, desalination processes and the literature related to DBPs formation in desalinated seawater and blended water were reviewed and their findings were summarized.

Chapter 4 presents the methodologies and models of exposure and risk analysis, and disability adjusted life year analysis from DBPs in desalinated and blended water. In this chapter, models to estimate human exposure and risk from THMs were described for multiple exposure pathways, such as ingestion of drinking water, and inhalation and dermal absorption during showering and bathing.

In Chapter 5, the DBPs data generated in this study and collected from literature were analyzed. DBPs variability was presented for different regions. The chronic daily intakes, cancer risks and disability adjusted life year (DALY) were predicted and discussed. Finally, the strategy of controlling DBPs exposure and risk was discussed.

Chapter 6 presents the summary of the outcomes of the thesis and discussed the limitations of this study.

Finally, Chapter 7 presents the recommended future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The chapter is divided into four segments. The first segment gives an overview of the chapter. The second segment describes the water resources available in Saudi Arabia, followed by the disinfection process in the third segment, which discusses the process of water disinfection and the chemistry of few disinfectants. In this segment, formation of disinfection byproducts (DBPs) due to disinfection process are also summarized with their possible effects to human health. Finally, the last segment summarizes the need for risk assessment from exposure to DBPs in desalinated and blended water.

2.2 Water Resources in Saudi Arabia

Saudi Arabia has limited resources of water. The water demands in different sectors (e.g., agriculture, domestic and industry) are satisfied by groundwater, surface water, desalinated water and treated wastewater. Among these sources, groundwater contributes the most, which is generally used in all sectors (e.g., agriculture, domestic and industrial). The surface water, which is the stored water from seasonal rainfall events, is typically used for recharging the groundwater aquifers, and domestic and agricultural uses. The desalinated water is primarily used for domestic purposes while the treated wastewater is used mainly for agriculture and landscaping purposes. The sources are briefly characterized below:

2.2.1 Groundwater Resources

Groundwater (GW) resources in Saudi Arabia are divided into two types: non-renewable or fossil GW in deep rock aquifers and renewable GW in the shallow alluvial aquifers. The non-renewable GW, which was composed about 10 to 32 thousand years ago, is confined in the limestone and sandstone formations with a thickness of about 300 m at a depth of 150 – 500 m [56]. The principle aquifers for non-renewable water are Riyadh, Dammam, Dhurma, Minjur, Neogene, Saq, Tabouk, Umm Er Radhuma, Wajid and Wasia [57,58]. Variable quantities of non-renewable GW in Saudi Arabia have been reported. The Ministry of Planning reported that the GW reserves were 338 billion cubic meters (BCM) with 500 BCM of probable reserves [59,60]. Few studies have indicated that the proven, probable and possible reserves of GW were 353.2, 405 and 705 BCM respectively [59,60]. The natural annual recharge to these aquifers was estimated to be 1.28 BCM [58,60], in which nearly 395 MCM/year is drained out from Saudi Arabia. It is likely that significant portion of this water might have been used in the past [5,57,60]. Some aquifers showed remarkable declines in water levels. For instance, the piezometric level in Minjur aquifer dropped from 45 to 75 meter beneath the ground surface over the period of 1965 – 1980 [61]. Similarly, a decline in water level took place for the Wasia aquifer [56]. In addition, during 1965 – 1975 and 1979 – 1981, water level in the Saq aquifer was reduced by 15 m in the east of Buraydah city, and by 5 meters near the middle of Buraydah city, respectively [56].

The renewable GW is stored in the secondary and/or shallow alluvial aquifers. These aquifers are usually unconfined, have a small area and water tables, which respond to local precipitations rapidly. These aquifers extend mostly over the southwestern region of Saudi

Arabia and have a variable thickness exceeding up to 100 m, with a width varying between 1 and 2 km. Some of the secondary aquifers are Aruma, Al-Jauf, Al-Jilh, Al-Khuff, Basalts, Sakaka, the lower Cretaceous, the upper Jurassic, and Wadi Sediments. Water from these aquifers shapes the main source in western Saudi Arabia. It is used for domestic and irrigation purposes, while it is the main source of drinking water in few areas. Although the renewable GW is limited in quantity, it can be replenished more recurrently and more rapidly than the fossil GW [62]. Table 2.1 shows the contributions of GW in various regions during 2009 – 2012.

Table 2.1: GW extraction in different regions of Saudi Arabia (MCM/year) [62–65]

Region	2009	2010	2011	2012
Riyadh	4623.9	4474.9	4368.9	4403.4
Makkah	1093.8	988.4	911.0	882.2
Madinah	1053.0	1011.0	979	941.3
Qaseem	2366.8	2274.7	2190.7	2116.7
Eastern Region	1212.4	1179.8	1030.2	983.5
Aseer	400.5	390.3	372.3	365.6
Hail	1404.0	1351.0	1300.5	1252.7
Tabouk	799.1	763.4	729.8	698.9
Al-Baha	124.0	112.8	100.2	76.1
Northern Borders	31.0	31.2	31.5	31.8
Al-Jouf	1559.0	1490.7	1425.6	1363.6
Jazan	1880.9	1755.7	1689.7	1611.1
Najran	294.0	285.7	278.4	271.7
Total	16842.4	16109.5	15407.8	14998.6

2.2.2 Groundwater Resources

Seasonal rainfall events are the sources of surface water (SW) in Saudi Arabia. In the northern part, annual rainfall varies between < 100 – 200 mm, while in the south, up to 500 mm/year rainfall is not uncommon [59]. The long-term average rainfall in the country was estimated to be approximately 100 mm/year, in which most of this rainfall occurs in the south and southwestern regions of the country [59]. The total runoff was approximated to be 2.2 BCM/year [66]. A portion of it infiltrates and recharges the shallow aquifers, whereas some of it evaporates [66]. In the western region, approximately 60% of total runoff occurs where the area represents only 10% of the total land area of the country,

while the remaining 40% occurs in the extreme south of the western coast (Tihama), which covers approximately 2% of the total land area [59].

To facilitate surface runoff storage and recharge, there are 449 dams across the country with storage capacity of approximately 2.0 BCM [5]. The regional details of these dams, their purposes and capacities are presented in Table 2.2. Among these dams, 390 dams with a capacity of approximately 1.5 BCM/year were constructed for GW recharges and control. A total of 57 dams store 453 MCM/year of water for drinking purposes, while 2 dams are used to store 51.5 MCM/year of runoff for agricultural purposes.

Table 2.2: Summary of dams, their purposes and storage capacities across Saudi Arabia (Capacity in MCM/year) [5]

Region	Distribution by purpose									
	Recharge		Flood control		Drinking		Irrigation		Total	
	No. of dams	Capacity	No. of dams	Capacity	No. of dams	Capacity	No. of dams	Capacity	No. of dams	Capacity
Riyadh	74	81.6	20	20.3	1	0.68			95	102.6
Makkah	34	62.3	11	670.8	4	44.0			49	777.1
Madinah	20	31.1	11	70.4					31	101.5
Qaseem	13	6.9	1	1.3	1	0.13			15	8.3
Eastern Region										
Aseer	66	370.2	18	17.8	29	62.3			113	450.3
Hail	35	22	3	1.8					38	23.8
Tabouk	10	7.2	2	3.7					12	10.9
Al-Baha	27	13.5	3	0.14	11	83.5	1	0.5	42	97.6
Northern Borders	8	20.9							8	20.9
Al-Jouf	5	6.6	5	8.0					10	14.6
Jazan	1	0.25	1	0.15	10	262	1	51.0	13	313.4
Najran	17	8	5	87.7	1	0.34			23	96.0
Total	310	631	80	882	57	453	2	51.5	449	2017.1

Table was generated using data of 2013 [5]

2.2.3 Desalinated Water

Saudi Arabia is the largest manufacturer of desalinated water (DW) as a single country. In 1980, the country produced approximately 7.7 MCM of DW [67]. During the period from 1980 to 2011, Saudi Arabia had a total of thirty operating desalination plants, located on the Arabian Gulf and the Red Sea coasts [7,67]. The Saline Water Conversion Corporation (SWCC) reported that the total production of DW in 2006 and 2009 was 1033 and 1055.1 MCM, respectively, which was increased to approximately 1476 MCM in 2011 [62,65,67]. The desalination plants in the country produced around 1070 and 1048 MCM desalinated water in 2004 and 2009, respectively and were projected to produce about 2070 MCM in 2014 [7]. The SWCC data showed that a total of fourteen plants have already served for more than 25 years of service lives. The country is planning to produce more DW by constructing additional plants in the near future [7,67]. The DW is mainly used for domestic activities in the major regions, such as Aseer, Eastern Region, Jazan, Makkah, Madinah, Qaseem, Riyadh, and Tabouk [52]. Noteworthy that the seawater desalination plants in Saudi Arabia satisfy more than 60% of the total domestic water demands in the country [63]. Generally, the DW is blended with treated GW and disinfected before supplying to the consumers [52]. The historical data of distributed DW in each region of Saudi Arabia are shown in Table 2.3.

Table 2.3: Distribution of DW in different regions of Saudi Arabia (MCM/year) [5,62–65,68]

Region	2007	2009	2010	2011	2012	2013
Riyadh	287.4	310.8	335.0	338.0	336	335
Makkah	370.7	443.0	539.0	613.0	639	670
Madinah	115.4	119.4	126.0	131.0	138	151
Qaseem	5.6	6.3	8.0	8.0	3	4
Eastern Region	250.4	208.1	187.0	316.0	343	332
Aseer	39.5	45.1	49.0	54.0	59	68
Hail						
Tabouk	6.2	8.1	9.0	10.0	10	10
Al-Baha						
Northern Borders						
Al-Jouf						
Jazan	0.6	0.9	5.0	6.0	18	25
Najran						
Total	1075.8	1141.7	1258.0	1476.0	1546	1595

2.2.4 Treated Wastewater

Treated wastewater (TWW) can be a potential source of water supply for agricultural, industrial and landscaping purposes. Reuse of TWW is in practice in many countries, including Saudi Arabia [59]. However, a major fraction of untreated and treated domestic wastewater are lost in Saudi Arabia through discharging into sand dunes, empty wadies or in the Arabian Gulf and Red Sea [52]. The Saudi government has encouraged the reuse of TWW for agriculture [62]. Reuse of TWW for agriculture can provide significant support toward achieving essential food sustainability.

There are 81 sewage treatment plants in Saudi Arabia in which domestic wastewater is treated [65]. The details of wastewater treatment plants, wastewater generation, TWW and reused TWW in different regions of the country are summarized in Table 2.4. The Ministry of Water and Electricity (MOWE) in Saudi Arabia reported that the annual capacity of these plants is approximately 1729.5 MCM [65], while the quantity of wastewater generation, TWW and recycled TWW in the country were approximately 2715.5, 1260.7 and 180.8 MCM, respectively [5]. This means, about 46.4% of the generated wastewater was treated; while only 14.3% of the TWW was recycled for reuse. Chowdhury and Zahrani (2013) [52] reported that more than 1500 MCM of domestic wastewater was produced in 2008, while around 730 MCM was treated. The MOEP (2010) of Saudi Arabia reported that about 325 MCM of TWW was reused in 2009, which is much greater than the values stated by MOWE.

Table 2.4: Details of wastewater treatment plants, wastewater generation, TWW and reused TWW in different regions of Saudi Arabia [5,65]

Region	Wastewater treatment plants		Wastewater generation		Treated wastewater (TWW)		Reused TWW			
	No. of plants	Design capacity (MCM/year)	Quantity (MCM/year)	Ratio to total quantity (%)	Quantity (MCM/year)	Ratio to total quantity (%)	Ratio to generation (%)	Quantity (MCM/year)	Ratio to total quantity (%)	Ratio to TWW (%)
Riyadh	13	345.8	808.3	29.8	350.8	27.8	43.4	49.5	27.4	14.1
Makkah	14	357.0	676.4	24.9	307.1	24.4	45.4	21.0	11.6	6.8
Madinah	1	109.5	177.8	6.5	59.4	4.7	33.4	1.1	0.6	1.9
Qaseem	5	52.6	120.1	4.4	52.6	4.2	43.8	16.4	9.1	31.2
Eastern Region	21	651.7	599.3	22.1	345.8	27.4	57.7	85.6	47.3	24.8
Aseer	18	133.8	76.0	2.8	68.9	5.5	90.6	4.2	2.3	6.1
Hail	1	4.4	32.1	1.2	6.2	0.5	19.3	0.1	0.1	1.6
Tabouk	1	21.9	98.9	3.6	43.8	3.5	44.3	1.1	0.6	2.5
Al-Baha										
Northern Borders	2	8.8	22.8	0.8	4.2	0.3	18.4	0.0	0.0	0.0
Al-Jouf	2	14.6	40.3	1.5	13.9	1.1	34.5	0.0	0.0	0.0
Jazan	2	7.5	38.9	1.4	6.8	0.5	17.5	1.7	0.9	25.0
Najran	1	21.9	24.5	0.9	1.2	0.1	4.9	0.1	0.1	8.3
Total	81	1729.5	2715.5	100.0	1260.7	100.0	46.4	180.8	100.0	14.3

2.3 Water Disinfection

2.3.1 History

The water disinfection process is considered as one of the most important public health developments in the 20th century [38]. It is the last treatment action for drinking water supplies and is performed to sustain a residual trace concentration of disinfectant in water distribution system [39]. In 1902, chlorination was first used as a water disinfectant in Middlekerke (Belgium) and in 1906, ozone was first used as a water disinfectant in Nice (France) [69]. In 1908, disinfection processes were first used in USA (Chicago and Jersey City) whereas in Canada it was first used in 1916 (Peterborough) [70,71].

2.3.2 Disinfectants and Disinfection Approaches

The most popular disinfectant to date is chlorine, which has been used to disinfect drinking water around the globe to protect public health. Besides, few other disinfectants, such as, chlorine dioxide, chloramine(s), ozone, potassium permanganate and ultraviolet irradiation are also used in several water supply systems. Table 2.5 presents a comparison among different disinfectants with respect to cost and efficiency. Chlorine has been the least costly disinfectant to date as well as very effective. However, the unintended formation of disinfection byproducts (DBPs) has been a major issue since their detection in drinking water in 1974 [30,72–74].

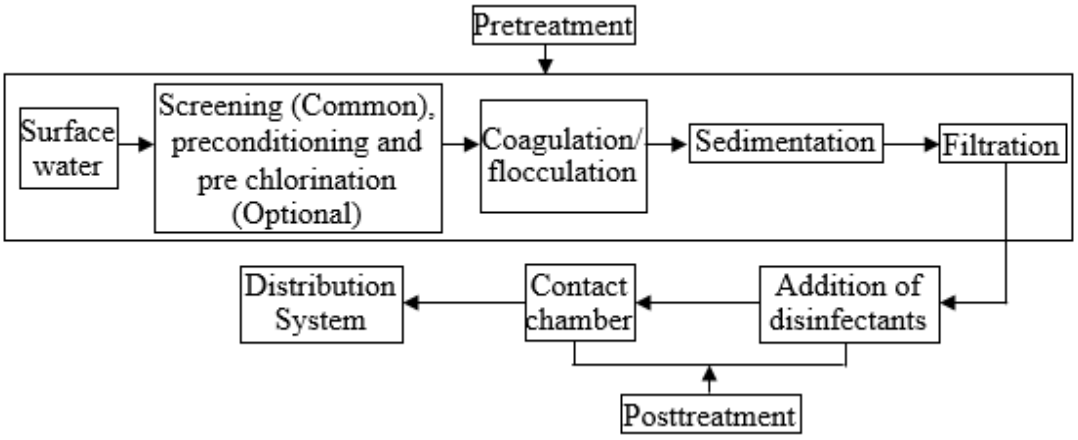
Table 2.5: Comparison of disinfectants [30,69,75–77]

Issues		Chlorine	Chloramine(s)	Chlorine dioxide	Ozone	Ultraviolet irradiation
Use		Very common	Common	Occasional	Common	Emergent
Cost		Very Low	Reasonable	High	High	Very high
Disinfection Efficiency	Bacteria	Very good	Good	Very good	Very good	Good
	Viruses	Very good	Fair	Very good	Very good	Fair
	Protozoa	Fair to poor	Poor	Good	Good	Very good
	Endospores	Good to poor	Poor	Fair	Very good	Fair
Organism regrowth		Less likely	Less likely	Likely	More Likely	More Likely
Byproducts	Regulated	HAAs and 4 THMs	HAAs and THMs	Chlorite	Bromate	None
	Unregulated	Many	NDMA, cyanogen halides	Chlorate	Biodegradable organic matter	None
Oxidation		Strong	Weak	Selective	Stronger	None
Removal of Odor and taste		Very good	Good	Very good	Good to Poor	None
Stability		Stable	Stable	Unstable	Unstable	Unstable
Free residual limit		4 mg/L	4 mg/L	0.8 mg/L		

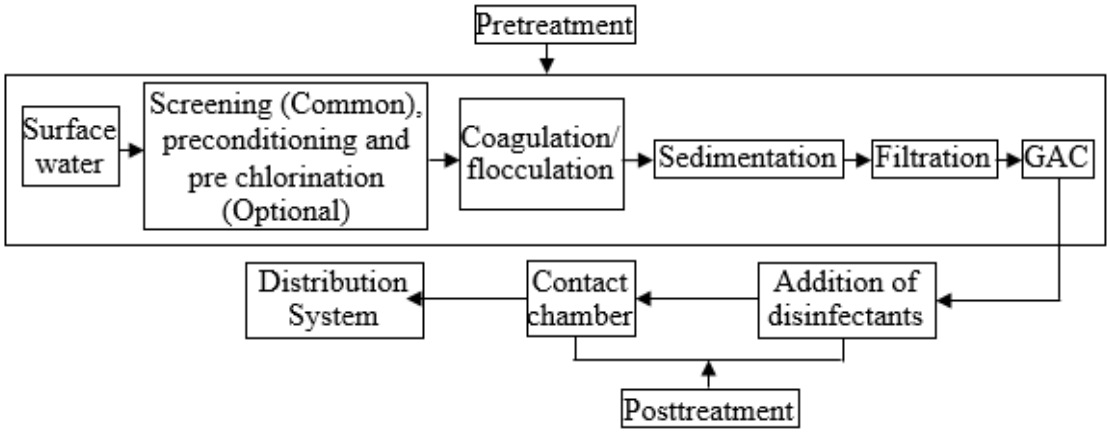
Table 2.5 demonstrates that chlorine and chloramine (s) are the two disinfectants, which provide stability of drinking water quality from source to tap. However, the oxidation status of chloramine(s) is relatively weak and it needs much more time to inactivate the microorganisms than chlorine. Further, chloramines are to be generated on-site, which increases the cost. There are many physicochemical and biological factors, which affect the efficiency of disinfection. The product of the concentration of residual disinfectant (C) and the time of contact (t) of the disinfectant in water is known as Ct value, which accounts for disinfection efficiencies. Generally, with the increasing value of Ct, the inactivation of microorganisms increases [69,78]. The Ct value is an important design parameter of disinfection processes, which varies with the type of disinfectant used [79]. Moreover, the operating condition of the treatment plant (pH, temperature), as well as the nature and types of microorganisms also affect the efficiency of disinfection [80]. Under the acidic condition, chlorine is more functional against microorganisms than alkaline conditions. Furthermore, it requires a lower Ct value to inactivate microorganisms in high water temperatures [81]. The required chlorine doses for disinfection are low in summer compared to that of winter conditions for a specific contact time. Conversely, within the water distribution systems, microbiological activities are lower in cold waters than warm waters [82]. In addition, the decay of residual disinfectant is rapid if the water temperature is high. It is very difficult to maintain a minimum residual in large water distribution system, especially at the remote points of the distribution systems during summer months. Higher doses of disinfectant are used in the summer months to maintain the minimum concentrations of disinfectant residuals in the distribution systems. But, a higher

concentration of disinfectant residuals and higher temperatures also affect the formation of DBPs in the distribution systems [83].

Several physicochemical processes, such as screening, coagulation, flocculation, settling, and filtration are followed in drinking water treatment and disinfection processes. From source waters, DBPs precursors (natural organic matter), pathogens and turbidity are reduced by employing different treatment methods [84–87]. Figure 2.1 shows a typical configuration of water treatment plant. Granular activated carbon (GAC) is added to conventional filtration method in the treatment system depending on the nature of organic matter present in the water (Fig. 2.1b). GAC is very effective in reducing NOM and other chemicals through catalytic degradation and adsorption; thus, minimizing the formation of DBPs [88]. However, introducing GAC in water treatment processes results in additional 30–50% cost in maintenance and operational purposes [89]. There is no low-cost treatment method available to date to remove pathogens and DBPs precursors completely [81,88,90].



(a) Conventional water treatment plant



(b) Water treatment plant with granular activated carbon (GAC)

Figure 2.1: A typical water treatment plant (modified after Chowdhury et al. [75])

In context to Saudi Arabia, chlorine is mainly used in disinfection and residual protection in water treatment processes and supply systems. It is also applied in different stages of water treatment as determined by the source water quality. For an example, the presence of phytoplankton and zooplankton in the source water can be increased by several folds during the summer time, which can cause biofouling during the treatment processes of the reservoir water. Application of chlorine during the pre-treatment of source water is often necessary for these plants. During disinfection process, most of the chlorine is exhausted due to reaction with NOM resulting in DBPs formation in drinking water. Past studies have showed that formation of THMs increases with the increase in pH and temperature [91,92]. However, the formation of HAAs were reported to increase with the decrease in pH [93–95]. It is important to determine the optimum range of pH for disinfection in the water treatment process as well as in the water supply systems.

2.3.3 Chemistry of Disinfectants

2.3.3.1 Chemistry of Chlorine

Chlorine gas does not dissolve according to Henry's law when introduced to water. It reacts with water rapidly to form hydrochloric acid and hypochlorous acid [69].

$$Cl_2(g) + H_2O \rightarrow HCl + HOCl \quad (2.1)$$

The hydrochloric acid ionized completely as it is a strong acid, results in reduction of alkalinity and pH [69].

$$HCl \rightarrow H^+ + Cl^- \quad (2.2)$$

In contrast, the hypochlorous acid is ionized in alkaline solution as it is weak acid [69].

$$HOCl \leftrightharpoons H^+ + OCl^- \quad (2.3)$$

pH and temperature play the major role in the distribution between hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). HOCl is better disinfectant than OCl^-. At pH 7 or lower, disinfection efficiency is better, as fraction of HOCl is much higher than OCl^- [96]. In pure water, chlorine is relatively stable. However, in drinking water, it reacts slowly with the naturally occurring organic matter, contributing a little to disinfection process [69]. The summation of HOCl and OCl^- are called the free chlorine. When ammonia (NH_3) is present in water, the successive reactions between chlorine and ammonia form 3 chloramine species: monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3) [69].

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad (2.4)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (2.5)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (2.6)$$

The summation of the three chloramine products is known as combined chlorine and the summation of free and combine chlorine is known as total chlorine. Equations 2.4-2.6 show the simple reactions between chlorine and ammonia when small quantities of chlorine are added to water. The reactions are illustrated in Figure 2.2. The figure is divided into four zones (offset, zone A, zone B, zone C). It requires a fraction of a second from the offset to reach Zone A. Here, the oxidizable substances, such as H_2S, MN (II), and Fe (II) are reduced. With the addition of chlorine, the total residual chlorine shows an increase of almost the amount of chlorine added until the molar ratio of chlorine to ammonia reaches

to unity, and the weight ratio of chlorine to ammonia nitrogen (NH_3-N) approaches to 5.07, assuming no other chlorine consuming species are present (Zone A) [69]. The residual present in this zone are mostly monochloramine, some dichloramine and traces of trichloramine [69]. The time of reaction in zone A varies from second to a few minutes [69]. In zone B, total residual chlorine decreases with the addition of chlorine (molar ratio> 1), due mainly to oxidization of few chloramine species. In this zone, the residuals are a combination of monochloramine and dichloramine, few free chlorine and some traces of trichloramine [69]. The reaction time of zone B varies from 10 to 60 minutes [69]. The beginning of zone C is called breakpoint. At that point, all the chloramine species are completely oxidized. In zone C, there are mostly free chlorine and trichloramine [69]. Generally, the breakpoint reaches when the weight ratio of chlorine to NH_3-N approaches around 7.0 [81]. The presence of organic nitrogen, dissolved organic matter, and reduced substances [e.g., S^{2-}, Fe(II), Mn(II)] in water influence the exact locations of breakpoint and maximum residual [69]. The zones, shown in the Figure 2.4, will shift to the right if any of these are present. The degree of shift depends on how easily the reducing substances are oxidized and stoichiometry of chlorine demand [69]. Beyond the breakpoint, with the addition of chlorine, the free-chlorine residual increases proportionately. Breakpoint chlorination is often used to remove ammonia in the water treatment processes. The free chlorine residuals are used for the residual protection and disinfection of drinking water. However, the formation of DBPs has become a major issue.

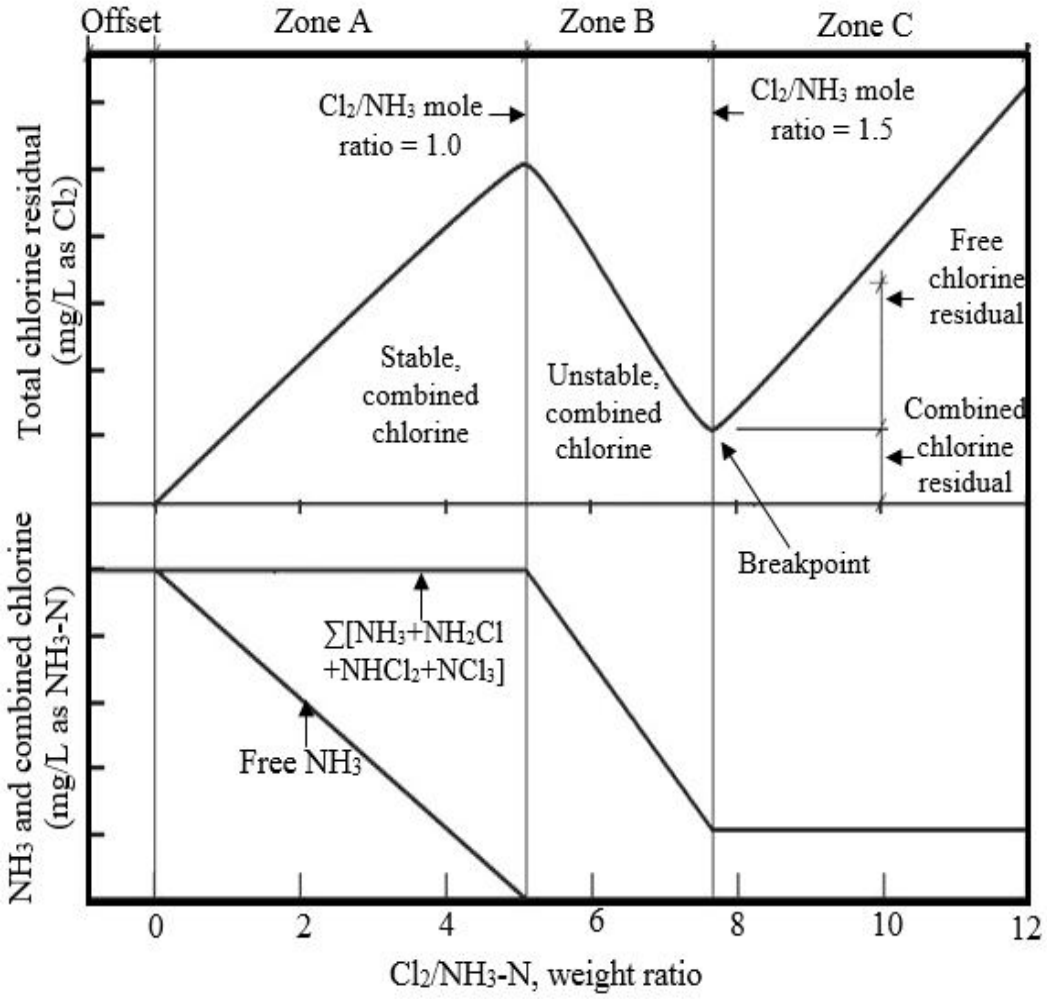


Figure 2.2: Overview of breakpoint chlorine stoichiometry

Adapted from MWH, 2005 [69]

In presence of bromide ion, hypochlorous acid reacts with bromide to produce hypobromous acid.

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (2.7)$$

The reaction to produce hypobromous acid is irreversible, and the product of the reaction i.e. hypobromous acid is a stronger halogenating agent than hypochlorous acid. It affects the general chemistry of chlorine. Hypobromous acid converts to Br_2, tribromine ion (Br_3^-), bromine chloride, or other halide complexes depending upon the pH and the nature of the predominant species present in water [97]. Bromanines can be formed if ammonia or organic amines are present in water, which decomposes readily to form nitrogen gas and bromide primarily [98,99]. Alkaline hypobromite solutions break to form bromate (BrO_3^-) and bromide (Br^-) when the water temperature is above 70ºC. These two anions are more stable thermodynamically.

$$3OBr^- \rightarrow BrO_3 + 2Br^- \quad (2.8)$$

Bromic acid and bromate are obtained by electrolytic oxidation of bromide solutions when chlorine is used as disinfectant. Both are powerful oxidizing agents, although the speed of their oxidation reactions is usually slow [100].

2.3.3.2 Further Details on Chemistry of Chlorine with NOM

During water treatment, when chlorine is dosed as a gas or as calcium/sodium hypochlorite, the major reactive form is hypochlorous acid (HOCl). Since hypochlorous acid is an electrophile, it tends to react with electron-rich moieties in NOM. The possible reactions pathways are electrophilic substitution, oxidation, and addition. The electrophilic attack is

significant in reactions with organics [101]. The second order reaction rate constant varies from 0.1 – 10^9 $M^{-1}s^{-1}$ [101], and chlorine reacts selectively with certain chemical functionalities. Amines, reduced sulfur moieties, and activated aromatic functionalities are highly reactive towards chlorine and have rate constants towards the upper end of the range. For instance, the apparent rate constant for the reaction between chlorine and the amino acid cysteine is ~6.2×10^7 at pH 7, due to the reactivity of a sulfur containing side group [102]. Hypochlorous acid also reacts rapidly with amines to produce chloramines. During the time span of disinfection, chlorine reacts too slowly with the less reactive moieties. For instance, reactions of HOCl with alkenes are typically too slow to be relevant during disinfection [103]. The speed of chlorine addition to alkenes can increase if the double bond is triggered by electron-donor groups. Similarly, reactions with alcohols are very slow e.g., the apparent rate constant of ~0 at pH around 7 for reaction with the monosaccharide ribose, but can lead to oxidation to ketones and aldehydes [104]. The reaction sites can be predicted based on the following descending order of reactivity: amides, carbonyls, other aromatics, double bonds << tertiary amines, phenols < primary and secondary amines < reduced sulfur groups [101].

Substances, including fulvic and humic acids, are major constituents of soil organic matter (e.g., humus). They are generally derivative of terrestrial vegetation and contain high lignin content. As lignin is aromatic, humic substances also tend to be aromatic [105]. This aromaticity confers high UV absorption and often color, and the ability to form supramolecular aggregates. Generally, the hydrophobic fractions of NOM are made up of humic substances. Electrophilic substitution occurs when chlorine reacts with aromatic compounds. For example, THMs are formed by stepwise chlorination at the 2, 4, and 6

positions of an ortho-para directing and electron-donating group such as phenol [106]**.** The major reactive sites within fulvic acids are reported to be the carbon between two hydroxyl groups or one hydroxyl and one O-glucoside group [74], with resorcinol being the most important THMs precursor. Boyce and Hornig [107] proposed a reaction mechanism for resorcinol, whereby electrophilic substitution of chlorine and a complex series of hydrolysis and decarboxylation reactions lead to the formation of trichloroacetic acid (TCAA) and chloroform. A simplified version is shown in Figure 2.3. Resorcinol-type structures were classified as fast-reacting THM precursors, while phenolic compounds were classified as relatively slow reacting THMs precursors [108]. This is also seen by comparison of rate constants of 0.36 and ~4×10^{3} M^{-1} s^{-1} for phenol and resorcinol respectively [108,109]. Resorcinol structures are thought to be commonly contained within macromolecular humic species in natural waters [110]. However, there is still inadequate information on the concentrations of these and similar compounds in drinking water. The reactivity of aromatic compounds can be explained in terms of electron-donating or electron-withdrawing influence of substituents [101]. The high reactivity of resorcinol is ascribable to having two activating ortho-para hydroxyl groups in the one and three positions.

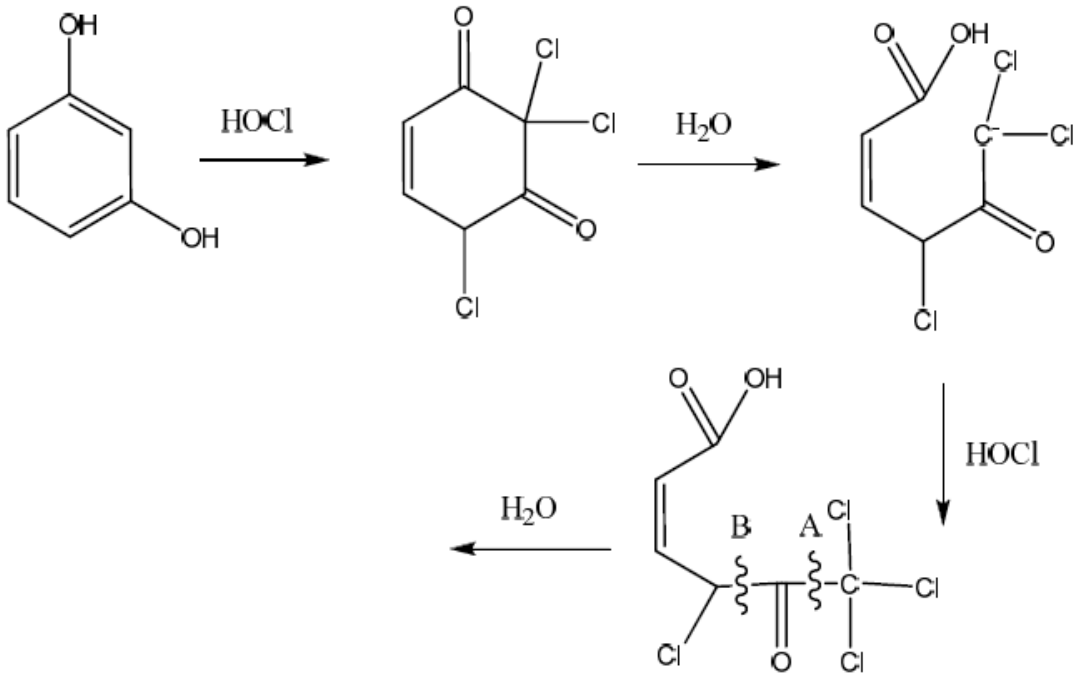
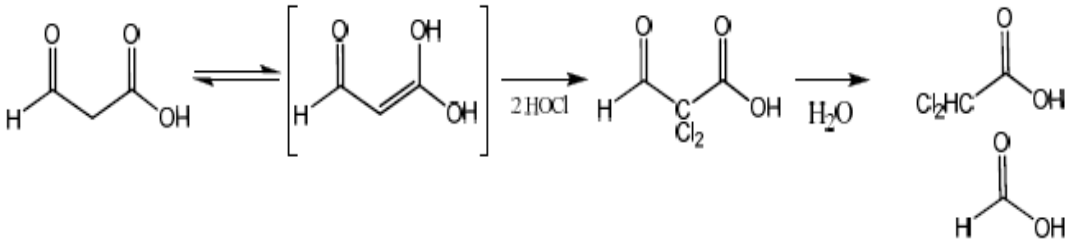


Figure 2.3: Chlorination of resorcinol

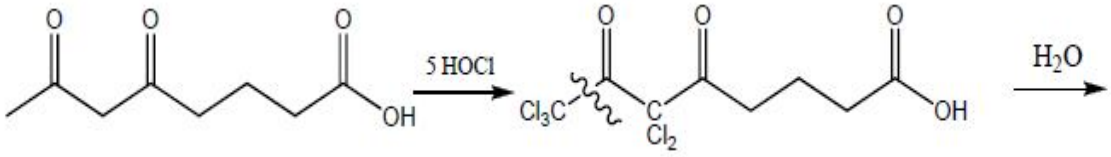
Cleavage at A will result in the production of $CHCl_3$ and cleavage at B will form TCAA

(adapted from Rook, 1977) [74]

In general, the simple carboxylic acids moieties are not reactive with chlorine (at pH 7.2, the rate constant of 2.3 M^{-1} s^{-1} with sorbic acid) [109], which also contains an alkene functionality. There is inadequate data about the existence of carboxylic acids in drinking water [111]. The NOM is primarily organic acids, rich in oxygenated functionalities [111], and under natural pH conditions, is anionic. The high charge density associated with hydrophobic and transphilic fractions of NOM [112,113] is a reflection of high carboxylic acid functionality. In particular, the transphilic fraction, with its high proportion of carboxylic acid functionality [114] may be an important precursor pool. With carboxylic acids, simple carbonyl groups react slowly, (negligible rate constant of chlorine with the steroid progesterone) [101]. Reaction with carbonyl groups normally proceeds through initial chlorine substitution at the α-carbon to the carbonyl group. With β-dicarbonyl species, the electron-withdrawing effect of both carbonyls makes the hydrogen groups attached to the α-carbon more acidic. DBPs can be formed by both acid and base catalyzed enolisation (Figure 2.4). The higher TCAA formation of fulvic acid isolates than humic acid isolates [115] might be linked to higher methyl ketone content, which could include β-dicarbonyl species. Base-catalyzed halogenation of β-dicarbonyls is dominant above pH of 5, and kinetically controlled by keto-enolisation [101]. Thus, it may be expected that increase in pH can elevate the DBPs formation from β-dicarbonyl species. A route, in which β-keto acids can give rise to dichloroacetic acid (DCAA) is shown for 3-oxopropanoic acid (Figure 2.4a). However, the formation of THMs is more complex. Figure 2.4b shows a possible route, in which 5, 7-dioxooctanoic acid could give rise to both DCAA and $CHCl_3$.



(a): Chlorination of 3-oxopropanoic acid



(b): Chlorination of 5,7-dioxooctanoic acid

Figure 2.4: Chlorination of carboxylic acids

Adapted from Dickenson et al., 2008[116]

The DCAA precursors are more hydrophilic than TCAA precursors [117] and that TCAA formation proceeds through intermediates common to THMs formation [115]. The explanation is thought to be that TCAA does not readily form from direct chlorine substitution of DCAA. Meanwhile, the formation of TCAA over $CHCl_3$ from a trichloroacetyl precursor structure is thought to be favored by the presence of conjugation capable of stabilizing the carbonium ions [86]. This information could suggest that DCAA precursors themselves are different to TCAA and THMs precursors.

In surface waters, the concentration of amino acids are generally around 0.3 mg/L [118], which is about 2 – 5% of the total dissolved organic carbon (DOC). These values can be higher in waters with the influence of wastewater or algal matter. The most common species of amino acids in water are aspartic acid, serine, glycine, and glutamic acid [118], which have low THMs formation potential (THMFP) and are relatively hydrophilic (log K_{OW} = -3.07 to -3.89) [106]. These are assumed to be within hydrophilic fractions of NOM. The concentrations of proteins and amino acids are linked to the levels of algae and wastewater effluent. The chlorine demand of amino acids can be theoretically calculated from the demand of constituent parts. Reactivity of chlorine with amino acids is high, with chlorine demand as high as 13 and 16 mol/mol for tyrosine and tryptophan respectively [119]. The respective THMFP for these amino acids is higher than other amino acids, and their chlorine demand is linked to the presence of aromatic or cyclic unsaturated side groups [119]. Similarly, side groups including amine, activated aromatic groups or sulfur groups are presumed to be the major precursor sites of linked amino acids. For simpler amino acids, high chlorine demand does not translate into more THMs formation. Further

details on the implications of different functional groups of NOM can be found in the literature [101,106,119–121].

2.3.3.3 Chemistry of Chlorine Dioxide

ClO_2 is highly soluble in water, particularly in cold water. ClO_2 remains as dissolved gas in solution and do not hydrolyze to any appreciable extent [122]. Several methods are used to produce chlorine dioxide (ClO_2) from chlorine. These include aqueous chlorine (HOCl), gaseous chlorine (Cl_2), and direct acid system using hydrochloric acid (HCl). Gaseous chlorine and 25 percent sodium chlorite ($NaClO_2$) solution is introduced by ejector in reaction column to form chlorine dioxide.

$$Cl_2(g) + 2NaClO_2 \rightarrow 2ClO_2(g) + 2NaCl \quad (2.9)$$

In the second method, chlorine gas is ejected to water form aqueous chlorine. Then sodium chlorite is introduced to form chlorine dioxide.

$$HCl \rightarrow H^+ + Cl^- \quad (2.10)$$

$$HOCl + 2NaClO_2 \rightarrow 2ClO_2 + Cl^- \quad (2.11)$$

In the direct acid system, $NaClO_2$ along with HCl are used. $NaClO_2$ reacts with HCl to produce ClO_2.

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2(g) + 5NaCl + H_2O \quad (2.12)$$

Chlorite (ClO_2^-) and chlorate (ClO_3^-) are the ClO_2 byproducts of concern [123]. ClO_2 does not generate organochlorine compounds as it reacts only by oxidation. ClO_2 is a moderately stable radical, contains chlorine in the +IV oxidation state, which does not undergo further reaction with water after it dissolves. It is believed that a mixed mechanism of oxygen atom-

transfer and electron-transfer steps are used by chlorine dioxide to react with most other species [81]. The following equations show the formation pathways of chlorate and chlorite when chlorine dioxide is used as disinfectant [81].

$$ClO_2(aq) + e^- \leftrightharpoons ClO_2^- \quad (2.13)$$

$$ClO_2^- + 2H_2O + 4e^- \leftrightharpoons Cl^- + 4OH^- \quad (2.14)$$

$$ClO_3^- + H_2O + 2e^- \leftrightharpoons ClO_2^- + 2OH^- \quad (2.15)$$

$$ClO_3^- + 2H^+ + e^- \leftrightharpoons ClO_2^- + H_2O \quad (2.16)$$

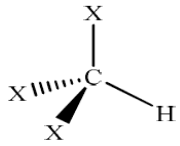
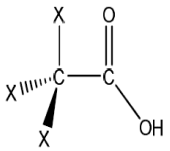
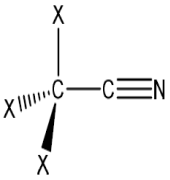
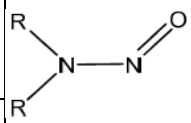
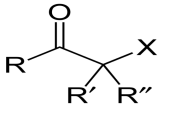
Several factors are associated with the production of chlorate ion including high concentrations of free chlorine at low pH, extremely high ratio of Cl_2 gas, dilute chlorite solutions held at low pH, an excess of hypochlorous acid and highly acidic reaction mixture etc. [124].

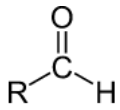
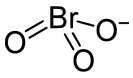
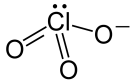
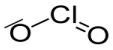
2.3.4 Disinfection Byproducts (DBPs)

During disinfection process, natural organic matters (NOM) reacts with disinfectant, such as, chlorine to form DBPs, some of which are toxic and pose threat to human health. To date, more than 100 different types of DBPs have been investigated while more than 600 types of DBPs are anticipated to be in drinking water [76]. The commonly reported DBPs in drinking water include haloacetic acids (HAAs), trihalomethanes (THMs), haloketones (HKs), haloacetonitriles (HANs), halonitromethanes, chlorite, chloramines (mono, di- and tri-), nitrosamines, bromate, nitro-phenol, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and MX homologues. In the recent years, emerging DBPs including iodo-THMs, N-nitrosodimethylamine (NDMA) have been found in drinking water. The drinking water systems using chloramines can have higher levels of NDMA, while NDMA

is considered a biomarker of bladder cancer [125,126]. Among different DBPs in drinking water, the most prevalent DBPs are THMs and HAAs [69]. High concentrations of these two contaminants have been detected after disinfection [76]. Table 2.6 shows the structures of few DBPs and the related disinfectants.

Table 2.6: Disinfectants and their DBPs

Class of DBPs	Compounds	MW	Acronym	Disinfectants	Structure
Trihalomethanes	Chloroform	119.38	$CHCl_3$	Chlorine	
	Bromodichloromethane	163.83	BDCM	Chlorine	
	Dibromochloromethane	208.28	DBCM	Chlorine	
	Bromoform	252.73	$CHBr_3$	Ozone, Chlorine	
Haloacitic acids	Monochloroacetic Acid	94.49	MCAA	Chlorine	
	Dichloroacetic Acid	128.94	DCAA	Chlorine	
	Trichloroacetic Acid	163.38	TCAA	Chlorine	
	Monobromoacetic Acid	138.95	MBAA	Chlorine	
	Dibromoacetic Acid	217.84	DBAA	Chlorine	
	Tribromoacetic Acid	296.74	TBAA	Chlorine	
	Bromochloroacetic Acid	173.39	BCAA	Chlorine	
	Bromodichloroacetic Acid	207.83	BDCAA	Chlorine	
	Dibromochloroacetic Acid	252.28	DBCAA	Chlorine	
Haloacetonitriles	Chloroacetonitrile	75.50	CAN	Chlorine	
	Dichloroacetonitrile	109.94	DCAN	Chlorine	
	Trichloroacetonitrile	144.38	TCAN	Chlorine	
	Dibromoacetonitrile	198.85	DBAN	Chlorine	
	Bromochloroacetonitrile	154.39	BCAN	Chlorine	
Nitrosamines	N-Nitrosodimethylamine	74.08	NDMA	Chloramine	
	N-nitrosodiethylamine	102.14	NDEA	Chloramine	
Haloketones	1,1,1-trichloropropanone	161.41	TCP	Chlorine	
	1,1-dichloropropanone	126.96	DCP	Chlorine	

Class of DBPs	Compounds	MW	Acronym	Disinfectants	Structure
Aldehydes	Acetaldehyde	44.05		Ozone, Chlorine	
	Formaldehyde	30.03		Ozone, Chlorine	
	Glyoxal	58.04		Ozone, Chlorine	
	Methyl glyoxal	72.06		Ozone, Chlorine	
Bromate		127.90		Ozone, Chlorine	
Chlorate		83.45		Chlorine dioxide	
Chlorite		67.45		Chlorine dioxide	

X = halogen group (Chlorine, bromine, iodine), R = alkyl or aryl group

The natural organic matter (NOM) in the source water is considered to be the primary precursor for DBPs formation in drinking water. Upon chlorination, NOM reacts with hypo-chloride to form DBPs. The characteristic equation to form DBPs is given below.

$$\text{NOM} + \text{Disinfectants} \rightarrow \text{DBPs} \tag{2.17}$$

Depending on the characteristics of NOM, DBPs formation can vary significantly. The fractions of NOM present in water are classified under humic acid, hydrophilic and hydrophobic substances [127–129]. The composition of the fractions of NOM is described in Table 2.7.

Table 2.7: Composition of NOM fractions

(Adapted from Sillanpää et al.) [130]

Fraction	Organic compound class	Reference
Humic acid	Fraction of humic substances that precipitates at pH 1	[131]
Hydrophobic acid	soil fulvic acids, C_5–C_9 aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols	[114,129, 132,133]
Hydrophobic base	Proteinaceous substances, 1- and 2-ring aromatics (except pyridine)	[129,132, 133]
Hydrophobic neutral	Aldehydes, amides, ketones, esters, >C_5 aliphatic alcohols, >C_9 aliphatic carboxylic acids and amines, >3-ring aromatic amines and carboxylic acids	[129,132, 133]
Hydrophilic acid	Combination of several hydroxy acids, polyfunctional carboxylic acids, <C_5 aliphatic carboxylic acids	[114,129, 132,133]
Hydrophilic base	Pyridine, amphoteric proteinaceous material (i.e., proteins, peptides <C9 aliphatic amines, amino acids, amino sugars)	[129,132, 133]
Hydrophilic neutral	Esters, carbohydrates, amides, polysaccharides, short chain aliphatic amines, ketones, cyclic amides, aldehydes, polyfunctional alcohols, <C_5 aliphatic alcohols	[129,132, 133]

Formation of THMs depends on the characteristics of source of water (NOM, DOC, TOC, UV_{254}), chemical (e.g., disinfectant) and operational parameters (pH, temperature, etc.). The hydrophilic acids, humic substances, and organic compounds are the primary precursors of THMs formation [134]. In addition, if bromide presents in the source water, the hypochlorous acid reacts with bromide ions to form hypobromous acid (pKa = 8.70), which is almost 15 times more reactive than the hypochlorus acid (pKa = 7.53). Consequently, the lighter Cl^- atoms are substituted by the heavier Br atoms, resulting in the formation of chloro-bromo THMs and other DBPs [117]. The hydrophobic fractions of

NOM with activated aromatic structure tends to produce higher THMs and HAAs than the hydrophilic fractions of NOM. In presence of bromide, formation of THMs is higher than HAAs, due mainly to hydrophilic fractions containing larger proportion of aliphatic structures, which are more reactive with bromide than the hydrophobic fractions. The activated aromatic structures are the main precursors of THMs and HAAs. But aliphatic structures define the fractions of THMs and HAAs. The pH plays an important role in DBPs formation. At pH of 8 or more, higher THMs are formed than HAAs, but the reverse happens at pH of 6. Figure 2.5 shows the possible process of THMs formation in the presence of bromide. HOCl has electrophilic chlorine species that react with electron rich locations in NOM, such as NOM having activated aromatic rings to form chlorinated THMs [135]. These fractions of NOM are generally hydrophobic. In presence of bromide, HOCl reacts with bromide to form HOBr. HOBr reacts with chlorinated THMs and heavier bromide ions replace relatively lighter chloride ions to form brominated DBPs. The reactivity of hydrophilic fractions of NOM with HOCl is very low but HOBr is more reactive to hydrophilic fractions of NOM rich in aliphatic structures [136]. Consequently, additional formation of brominated DBPs are expected.

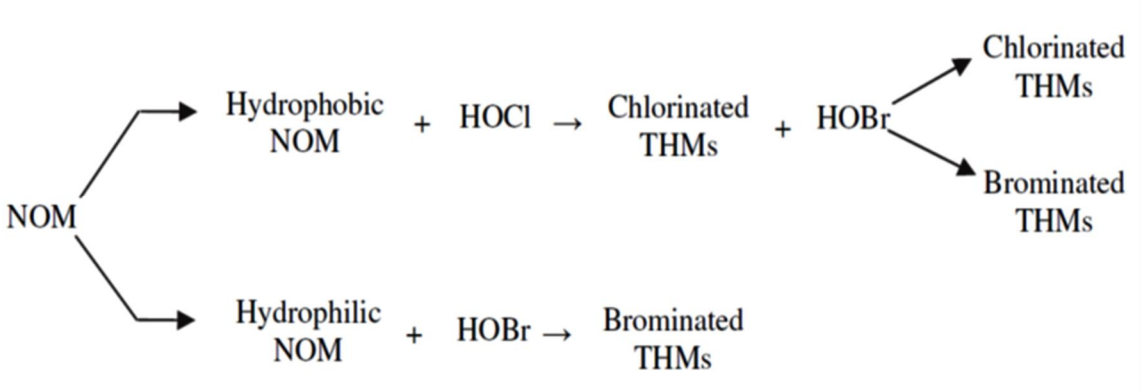


Figure 2.5: THM formation in the presence of bromide

2.3.5 Health Effect of DBPs and Regulatory limits on DBPs

Through considerable efforts within epidemiological and toxicological studies, it has been reported that there are possible adverse health effects from exposure to few DBPs. These DBPs are of major concern because of potential cancer risks to human and other chronic/sub-chronic health effects, such as stillbirth, pre-term delivery, miscarriage, cardiac anomalies, and low birth weight [31,33,137–139]. Table 2.8 summarizes the harmful effects of some of the main DBPs.

Table 2.8: Health effects of major DBPs [139]

Class of DBPs	Compound	Type	Potential Health Effects	R_fD (mg/kg/day)	SF (per mg/kg/day)
Trihalomethanes (THMs)	$CHCl_3$	B-2	Cancer, liver, kidney and reproductive effects	0.01	$CHCl_3$ is no longer considered to be a human carcinogen through oral route. Currently, under reassessment.
	DBCM	B-2	Reproductive effects, kidney, liver, and nervous system effects	0.02	0.062
	BDCM	B-2	Reproductive effects, kidney, liver effects, and cancer	0.02	0.0079
	$CHBr_3$	C	Kidney, liver, nervous system effects, and cancer	0.02	0.0084
Haloacetic acids (HAAs)	DCAA	B-2	Cancer, reproductive, developmental effects	0.004	0.05
	TCAA	C	Developmental, spleen, kidney, and liver effects	0.067	0.02
Nitrosamines	NDMA	B-2	Internal Bleeding, liver cancer, lung cancer		51
Bromate		B-2	Increased risk of Cancer	0.004	0.7
Chlorite		D	Anemia; nervous system effects	0.03	Not evaluated

C: Possible human carcinogen; B-2: Probable human carcinogen; D: Not classified; SF: Slope factor, upper bound lifetime probability of an individual's developing cancer as a result of exposure to potential carcinogen $(mg/kg\text{-}day)^{-1}$; R_fD: Reference dose, used to estimate non-carcinogenic effects resulting from exposure (mg/kg-day).

The possible health effects of DBPs have pressed many countries and organizations to establish guideline values (e.g. maximum levels) on DBPs concentrations in drinking waters. Several organizations, such as, European Union (EU), Health Canada (HC), World Health Organization (WHO), United States Environmental Protection Agency (USEPA) have set the regulatory limits of DBPs, which establish a foundation for the countries around the world to promulgate their regulations on these byproducts. Table 2.9 summarizes the guideline values of DBPs that are currently endorsed by different organizations.

Table 2.9: Regulatory limits on DBPs in µg/L in drinking water [12,139–142]

Class of DBPs	Compound	HC 2014	WHO 2011	NZ 2008	USEPA 2016	AUS 2016	UK 2010
Trihalomethanes	$CHCl_3$	100	300	400	80	250	100
	DBCM		100	150			
	BDCM		60	60			
	$CHBr_3$		100	100			
Haloacetic acids	DCAA	80	50	50	60	100	
	MCAA		20	20		150	
	TCAA		200	200		100	
	MBAA						
	DBAA						
Haloacetonitriles	DBAN		70	80			
	DCAN		20	20			
Aldehydes	Formaldehyde	None	None			500	
Nitrosamines	NDMA	0.04	0.1			0.1	
Cyanogen halides	Cyanogen chloride		None	400		80	
Chloral hydrate			None			20	
Bromate		10	10	10	10	20	10
Chlorate		1000	700	800			
Chlorite		1000	700	800	1000	800	

USEPA: United States Environmental Protection Agency; UK: United Kingdom; AUS: Australia; NZ: New Zealand; HC: Health Canada; WHO: World Health Organization

2.4 Risk Assessment of DBPs

Even with the huge number of research articles that have been published on DBPs, there are many scientific questions that need specific answers [27]. Disinfection is a necessary process to control microbial contamination in drinking water. But, during this process DBPs form unintentionally. So, question arises to limit DBPs formation considering the safety against microbial contamination. In order to provide a guideline value, health risk from exposure to DBPs must be evaluated. The USEPA and other groups have used the risk assessment tools in analyzing the potential health effects of DBPs [30]. The regulated DBPs were assessed several times using the methodologies stated in the Stage 2 D/DBP Rule [30]. These set of risk assessments tools reflected the concerns that were growing for reproductive and developmental effects associated with DBPs exposure. These assessment tools also combined the novel methods to estimate cancer risk. These newer methods highlight the maximum use of reliable data rather than depending on the default measures. The cancer guidelines categorize the method of actions for critical information required to determine if data are applicable to humans and the approach for the dose–response assessment is applicable.

CHAPTER 3

DBPS IN DESALINATED WATER

3.1 Introduction

There are six segments in this chapter. The first segment provides an overview of the chapter. The second segment discusses various desalination processes. The third segment discusses the formation of disinfection byproducts (DBPs) in different stages of desalination followed by DBPs formation in blended water. The fifth and sixth segment discuss the formation of DBPs in water distribution systems and plumbing premises of desalinated and blended water.

3.2 Desalination Process

The statistics in the “Introduction” chapter demonstrate the importance of desalinated seawater in satisfying domestic water demands in many regions of the country. The treated groundwater and desalinated water are blended, pH adjusted, disinfected and protected through residual disinfectants to ensure public health safety against microbial contamination. In the desalination processes, salts are separated from seawater to produce nearly salt-free freshwater by concentrating the salts in the rejected brine stream. Desalination processes are classified into two groups: thermal processes and membrane separation processes. The thermal separation method, also known as thermal distillation, is the oldest method, in which steam is collected by boiling seawater. Thermal distillation

processes are of three types: multistage flash distillation (MSF), vapor compression (VC), and multiple effect distillation (MED) while the MSF desalination processes are dominant in many countries. The most common membrane separation technique is the reverse osmosis (RO) process of desalination. In the RO process, water is isolated from a forced saline solution through a water-permeable membrane. Thermal desalination is the first choice in the Middle East countries. The major causes of using thermal process are the inferior quality of local feed water and availability of fossil fuel resources. In addition, the feed water has high fouling potential on membrane systems characterized by high salinity and high temperature [63]. The basic procedures of the most common thermal process (MSF) and membrane separation process (RO) are summarized below:

3.2.1 Multistage Flash Distillation (MSF) Process

In the MSF desalination processes, seawater is heated while passing through multiple heating stages. In the heating stages, there is a brine recirculation system, which includes heat recovery units and heat denial units. Figure 3.1 illustrates a schematic diagram of a MSF desalination process.

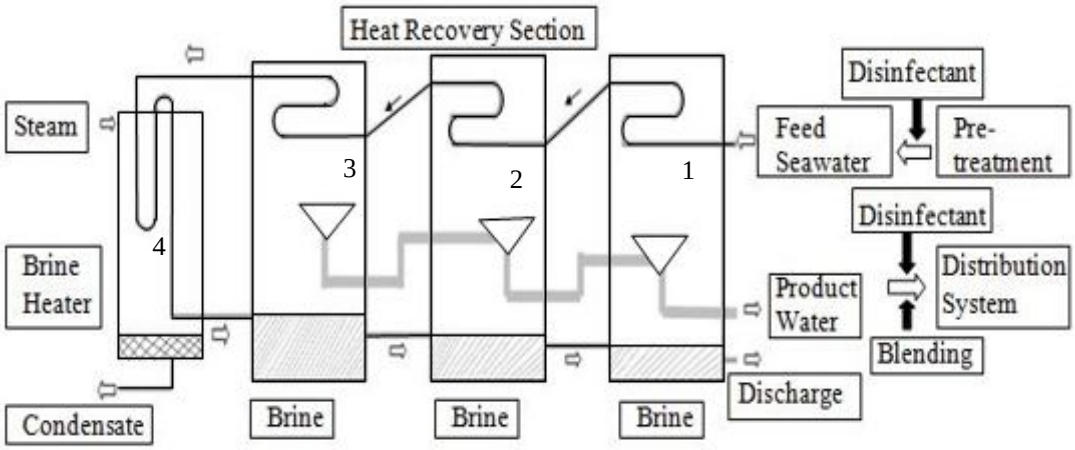


Figure 3.1: Schematic diagram of multistage desalination (MSF)

In this process, pressure decreases from the first (1) to the last (4) chamber. The first chamber is introduced to seawater and heated by brine heater. The surrounding pressure of the first chamber is lower than that in the brine heater, leading to the formation of steam of a fraction of seawater. The residual water is sent to a series of supplementary stages with increased vacuum pressure. The vapor is condensed into fresh water and collected as potable water. The heat produced through condensation of vapor is generally recycled and reused to pre-heat the cold seawater.

3.2.2 Reverse Osmosis (RO) Desalination Process

The RO process is the widely used method for desalinating seawater in many countries, including, Saudi Arabia, Bahrain, Jordan, Algeria, Australia, UAE, Egypt, USA etc. [143–147]. Generally, seawater RO plants function with one, two or four RO passes subjected to the design constraints and freshwater regulations.

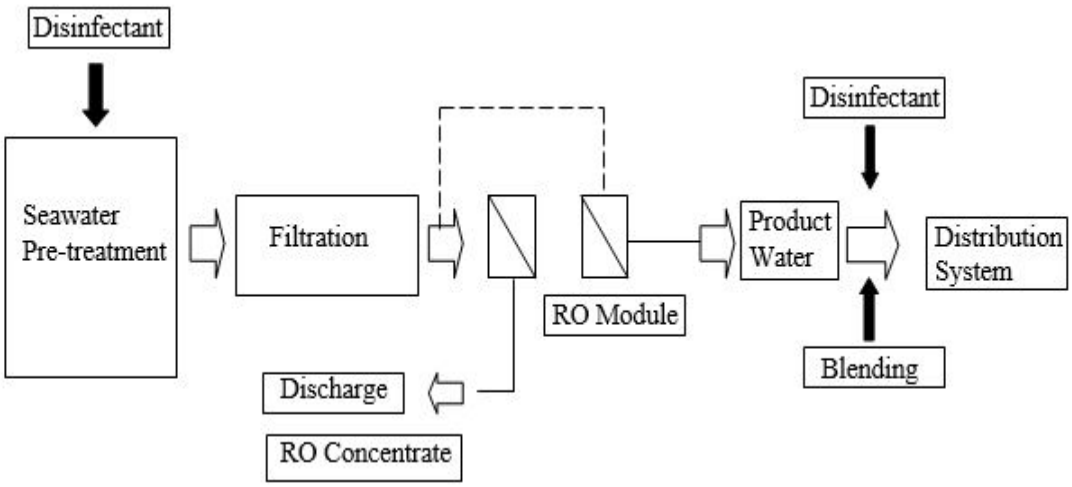


Figure 3.2: Schematic diagram of reverse osmosis (RO) desalination process

Figure 3.2 shows a schematic diagram of an RO desalination process. In the RO process, water is separated from a pressurized saline solution using a water-permeable membrane. Usually, the feed water passes through several membranes to extract the maximum amount of water. The seawater requires pre-treatment to remove the larger particles and bio-fouling agents before passing through the RO process. To control the damage of membrane materials, residual chlorine is reduced in the pre-treated seawater by using dechlorinating or reducing reagents, such as sodium bisulfate. To increase the efficiency of membrane, anti-foaming and anti-scaling chemicals are also used. Generally, the concentrations of DBPs in RO permeate are higher than the thermal distillate, which depends on the rejection efficiency of RO membranes.

3.3 Formation of DBPs in Different Stages of Desalination

3.3.1 Formation of DBPs during Pre-treatment

Generally, seawater or brackish water is used as feed water for desalination. The salinity of brackish water is more than freshwater but less than seawater. Brackish water is found in estuaries, the point where rivers meet the sea and in the aquifer of coastal areas. The feed water is collected from seawater intakes. The most common intakes are surface intakes, subsurface intakes, beach wells and infiltration galleries [148]. Surface intakes may be the dredged channels through the surf zone. Seawater is drawn to surface intakes from lagoons or enclosed bays [148]. The lagoons/enclosed bays are protected by a reef or a barrier island from shore to surf zone [148]. Subsurface intakes collect water from on-shore coastal aquifers [149]. Beach wells are two types: vertical beach wells and vertical beach wells with horizontal extensions [148]. Vertical beach wells are suitable for treatment plant of small capacity but with horizontal extensions, it can be used for large-scale treatment plants [149]. Infiltration gallery intakes are also known as under-ocean floor seawater intakes or seabed infiltration systems. It is a series of slow sand media filtration beds in the near-shore surf zone submerged at the bottom of the ocean [149]. The allowable particle size in feed water varies depending on the methods of desalination [150]. The allowable particle size is given in Table 3.1 for different desalination techniques.

Table 3.1: Allowable particle size in feed water [150]

Technologies	Max. Particle Size	Examples
Multi-Stage Flash (MSF)	1/3 of inner diameter of the tube	5 mm for 15 mm tube, 15 mm for 45 mm tube
Multi-Effect Desalination (MED)	1/3 of inner condenser tubes diameter	4 mm for 12 mm tubes, 8 mm for 24 mm tube
MED + Vapor Compression		for spray nozzles: 0.5 mm
Reverse Osmosis (RO)	SDI value < 3.5; 5–20 μ	

SDI: Silt density index, measures the fouling capacity of water in reverse osmosis systems.

To prevent microbiological contamination and biofouling, disinfection of seawater and product water is necessary for desalination plants. Concentrations of DBPs during pretreatment depend on the type and doses of disinfectant used, pH, temperature, contact time, and the inorganic and organic contaminants in the source water [10,16,151]. The most common pretreatment process of seawater prior to desalination is continuous or intermittent chlorination. Pretreatment is essential to prevent biofouling in the intake structures and on membranes in RO process. The initial doses of chlorine vary in the ranges of 0.5 – 2.0 mg/L and the typical target residuals are 0.25 – 0.5 mg/L. The residual chlorine helps coagulation process, to control algae problems in sedimentation basins, to reduce odor problems, and to prevent mud-ball formation in filters. The common and abundant DBPs in chlorinated water are THMs and HAAs [152]. In chlorinated seawater, brominated species are predominant in both HAAs and THMs. If chloramines are used as an alternative disinfectant, lower amounts of HAAs and THMs are formed [65-66]. However, more toxic compounds, such as, nitrosamines can be formed during chloramination. The toxicity of the new groups of DBPs from chloramination is not well understood to date. Chlorine

dioxide (ClO_2) does not produce considerable levels of THMs and HAAs while it can produce chlorite (ClO_2^-) and chlorate (ClO_3^-). Ozone is not typically used as a disinfectant for seawater because of higher levels of bromide in seawater, which can form bromate (BrO_3) with regulatory limit of 10 µg/L [67-68]. DBPs found in the chlorinated seawater of desalination plants, cooling effluents of coastal power plants and in several lab studies are presented in Table 3.2. DBPs produced in the seawater treated with alternative disinfectants such as ozone, chlorine dioxide, chloramine(s) are also presented in Table 3.2.

Table 3.2: DBPs during pretreatment of seawater

Location	Disinfectant	THMs (µg/L)	HAAs (µg/L)	HANs (µg/L)	Other DBPs (µg/L)	Dose (mg/L) and Contact time	Reference
Feed water of desalination plants							
Red sea coast, Saudi Arabia	Chlorine	6.18-18.41	5.35-6.86 (HAA9)	0.43-0.76 (DBAN)	1.90-2.57 (I-THMs)	0.25-0.5 (residual)/0.7-1.0 (continuous)	[17]
Al-Jubail, Saudi Arabia		ND	7.0 (HAA5)			1.0 (residual), 24 h	[153]
Jeddah, Saudi Arabia		3.3-24.0	ND				[154]
Eastern Coast, Saudi Arabia		3.1-27.9	ND			2.0 (residual)	[16]
Umm AL Nur, UAE		78-95	ND			0.5-2.0(residual)	[155]
Ruwais, UAE		<25	<14.5 (HAA5)			0.2-0.25, 10-15 min	[156]
Shuwaikh, Shuiaba, Doha, Kuwait		21.7-61.4	ND				[157]

Location	Disinfectant	THMs (µg/L)	HAAs (µg/L)	HANs (µg/L)	Other DBPs (µg/L)	Dose (mg/L) and Contact time	Reference
Okinawa, Japan		35	ND			0.3	[18]
Ebara Corp, Japan		15-25	ND			0.2-0.3 (residual)	[158]
Carlsband, USA		3.0-52	9.5-19 (HAA9)	0.5-1.9	0.3-0.6 (Br-phenols)	0.5-2.0 (initial), 2 h	[21]
Tampa Bay, USA		490-680	69-175 (HAA5)			2.5-5.0	[13]
Lab studies with seawater							
Al-Jubail, Saudi Arabia	Chlorine	80	ND			10.0, 72 h	[16]
Doha, Qatar		60-165	ND			1.0-4.0, 168 h	[10]
Barcelona, Spain		154	ND			1	[159]
Aquaria, undisclosed		ND	<122 (HAA9)			1.0-3.0, 30 min	[19]
North sea coast, Norway		ND	3.2-6.3 (HAA4)			0.7-3.5 (Cl_2 /DOC), 24 h	[15]
Seattle, USA		107	99(HAA9)	4.0 (DCAN, BCAN)		1.0, 8 h	[160]

Location	Disinfectant	THMs (µg/L)	HAAs (µg/L)	HANs (µg/L)	Other DBPs (µg/L)	Dose (mg/L) and Contact time	Reference
Florida, USA		43-206	39-75 (HAA9)			2.0 (Cl_2 /DOC), 24 h	[161]
Al-Jubail, Saudi Arabia	Chloramine	35	ND			10.0, 72 h	[153]
Busan, Korea	Chlorine dioxide	ND	0.4-2.5 (HAA5)			0.2-10.0, 72 h	[162]
Barcelona, Spain		0.34	ND			0.2-0.4	[159]
Al-Jubail, Saudi Arabia	Ozone	180 (TBM)	ND	ND		5.0, 72 h	[153]
Halifax, Canada		22-33	ND		500-4500 (bromate)	0.4-3.9	[163]
Aquaria, undisclosed		ND	61(TBAA)		16.5-34.8(HNMs)	1.0-3.0, 15 min	[19]
Cooling effluent of power plants							
North sea coast, France	Chlorine	7.7-26.8 (TBM)	7.3-10.2 (DBAA)	0.9-3.6 (DBAN)	0.1-0.4 (Br-phenols)	0.2-0.77	[164]

In chlorinated seawater, the concentrations of HAAs and THMs had the ranges of ND – 175 µg/L and ND – 680 µg/L, respectively. Among which, most of the cases, the concentrations of THMs are below 100 µg/L (Table 3.2). Seawater oxidized with alternative disinfectants have low levels of THMs (ND – 180 µg/L) (Table 3.2). Some other DBPs such as HANs, HNMs, Br-phenols, I-THMs, bromate were also reported (Table 3.2).

3.3.2 Formation of DBPs Prior to Distribution in Desalination Plants

In thermal desalination plants, the chance of DBPs remaining after distillation is very low, which is unlikely to be affected by the DBPs formed in the disinfected seawater. Seawater RO plants often function with one, two or four RO passes which depend on the desired water quality standard and design parameters [69-71]. In comparison with thermal distillate, the concentrations of DBPs are higher in RO permeate [10]. The performance of rejection of membrane in RO process determines the concentration of DBPs in RO permeate [10]. On RO membranes, biofouling may occur due to adsorbtion and accumulation of reactive organic matter in the fouling layer. Consequently, it can lead to the formation of THMs and HAAs in the RO permeate. In thermal distillate and RO permeate of pilot plants and desalination plants, occurrences of DBPs were reported. Chlorine was used as disinfectant for pretreatment of seawater in most cases, and mostly THMs were measured and reported. The concentrations of THMs in the thermal distillate were in the ranges of 0.09 – 22.8, whereas for RO permeate, the concentrations were in the ranges of 0.36 – 72.95 µg/L. Concentrations of HAAs were in the ranges of ND – 1.6 and ND – 6.1 µg/L respectively (Table 3.3).

Table 3.3: DBPs in desalination plants

Location	THMs (µg/L)	HAAs (µg/L)	HANs (µg/L)	Other DBPs (µg/L)	Reference
Thermal Distillate					
Red sea coast, Saudi Arabia	0.38	ND	0.45 (DBAN)		[17]
Al-Jubail, Saudi Arabia		1.6 (HAA6)			[153]
Jeddah, Saudi Arabia	0.17-0.55				[154]
Eastern Coast, Saudi Arabia	0.09-3.48				[16]
Jazan, Saudi Arabia	2.3-2.7				[165]
Kuwait	2.7-22.8				[157]
RO permeate					
Red sea coast, Saudi Arabia	0.36-66.7	ND-0.71	ND-1.98 (DBAN)	1.74-2.64 (I-THMs)	[17]
Jeddah, Saudi Arabia	12.2-39.0				[154]
Jazan, Saudi Arabia	14.2				[165]
Makkah, Saudi Arabia	8.5				[165]
Qatar	3.99-72.95				[166]
Carlsbad, USA	ND-6.7	2.1-6.1	0.58-0.79		[21]
Tampa Bay, USA	2.3-6.4	1.0-2.5			[13]
Okinawa, Japan	2.7				[18]
Ebara Corp, Japan	2.0-3.0				[158]

3.3.3 DBPs Formation in Distribution Systems Desalination Plants

Desalinated waters need stabilization prior to supplying in the distribution network, which is often performed by blending with the treated brackish well water or untreated seawater. The stabilization is performed to reduce metal corrosion and concrete dissociation by the product water. The water quality parameters of MSF and RO desalination plants are presented in the Table 3.4-3.5.

Table 3.4: Water quality parameters of RO permeate of Yanbu SWRO plant, Saudi Arabia [167]

Parameter	Value
pH	5
Total dissolved solids (mg/l)	<500
Cl^- (mg/l)	<250
SO_4^{2-} (mg/l)	15
HCO_3^- (mg/l)	3
Na^+ (mg/l)	135
K^+ (mg/l)	6
Ca^{2+} (mg/l)	3
Mg^{2+} (mg/l)	6

Table 3.5: Water quality parameters of product water of Yanbu MSF plant, Saudi Arabia [167]

Parameter	Value
Temperature (ºC)	25-32
pH	8-8.5
Residual chlorine (mg/L)	1
Turbidity (NTU)	0.5
Total Alkalinity (mg/L as $CaCO_3$)	40
Carbonate Hardness (mg/L as $CaCO_3$)	80
Calcium Hardness (mg/L as $CaCO_3$)	40
Carbon dioxide (mg/L as CO_2)	40
Dissolved oxygen (mg/L)	7
Total Dissolved solids (mg/L)	30
Langelier Saturation Index	0.1-0.3

The RO permeates generally have low level of dissolved organic carbon (DOC), typically in the range of <0.1 – 0.6 mg/L [13,21]. However, bromide (Br^-) and iodide (I^-) concentrations in the RO permeates were in the ranges of 250 – 600 and <4 – 16 µg/L) respectively, which are much higher than many freshwater sources and are high enough to enhance brominated and iodinated DBPs formation in water [13,14,18,21]. During the post-disinfection protection in the water distribution systems, application of chlorine form hypobromous acid (HOBr) at pKa of 8.7, which is a better substitution agent than hypochlorous acid (for HOCl, pKa = 7.5) [168].

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (3.1)$$

Due to the higher reactivity of HOBr, relatively lighter chloride ions are replaced by the heavier bromide ions and thus, DBPs amount increases. Further, brominated DBPs are

reported to be more toxic to human health than the chlorinated DBPs [139]. DBPs in the distribution system of desalination plants are shown in Table 3.6.

THMs in the distribution systems of desalination plants of Jeddah and Doha were reported to be in the range of 13.5 – 25.7 μg/L, 0.37 – 8.15 μg/L respectively, in which brominated THMs were the dominant species. The cities, supplied with desalinated water only, had much lower THMs than the cities supplied with blended water. In recent studies, THMs and HAAs in the blended water (desalinated water + groundwater disinfected with HOCl) were observed to be in the ranges of 5.0 – 91.0 and 5.1 – 52.0 μg/L respectively [169]. In addition, higher levels of bromate were also reported in the blended water from different places in Saudi Arabia [170].

Table 3.6: DBPs in distribution system of desalination plants

Location	DBPs	Range (μg/L)	Mean (μg/L)	Reference
Jeddah RO Water line	$CHCl_3$	0.03-0.06	0.05	[171]
	CCl_4	0-0.01	0.005	
	BDCM	0.6-0.46	0.15	
	DBCM	0.27-0.78	0.49	
	$CHBr_3$	13.06-24.7	18.27	
	TTHMs	13.46-25.68	9.47	
Distillate received in Doha blending plant, Kuwait	$CHCl_3$	0.00-0.53	0.05	[172]
	BDCM	0.0-1.95	0.35	
	DBCM	0.0-0.9	0.17	
	$CHBr_3$	0.21-5.92	1.75	
	TTHMs	0.37-8.15	2.33	

3.4 DBPs Formation in Blended Water

The RO permeates are blended with treated groundwater, which typically has higher DOC concentrations, leading to the higher concentrations of DOC in the blended water. As a result, the blended water typically has higher levels of bromide and DOC, which accelerate brominated DBPs formation upon chlorination. THMs in the blended potable water were reported to be in the range of 9.25 – 36.33 μg/L, in which brominated THMs were the dominant species (Table 3.7).

Table 3.7: DBPs in blended water

Location	DBPs	Range (μg/L)	Mean (μg/L)	Reference
Desalination plant				
Jeddah SWRO/MSF plant, Saudi Arabia	$CHCl_3$	0.0-0.24	0.08	[154]
	CCl_4	0-0.01	0.008	
	BDCM	0-0.29	0.14	
	DBCM	0.24-0.74	0.36	
	CHBr3	3.85-29.38	8.92	
	TTHMs	9.25-30.12	9.47	
Doha blending plant, Kuwait	$CHCl_3$	0.-3.8	0.88	[172]
	BDCM	1.17-3.83	2.34	
	DBCM	2.65-11.27	6.25	
	CHBr3	5.0-19.63	10.96	
	TTHMs	10.53-36.33	20.42	
Lab Studies with chlorine dose 5 mg/L and contact time 24 h				
Blending ratio 1:2	TTHMs		42.6	[22]
Blending ratio 1:5	TTHMs		40.5	
Blending ratio 1:10	TTHMs		29	

3.5 DBPs Formation in Water Distribution System

The blended water with free residual chlorine is pumped into the water distribution networks. The water can stay in the distribution networks for few hours to several days. During this period, additional DBPs can be formed. Past studies have reported higher concentrations of DBPs in the water distribution networks that those in the water treatment plants (Table 3.8). Within the eight major cities in Saudi Arabia (Dammam, Riyadh, Makkah, Madinah, Jeddah, Abha, Hail, Buraydah), THMs were in the range of 0.03 – 41.7 μg/L. In Kuwait, Qatar and Egypt, the concentration of THMs were higher, in the range of 8.39 – 92.35 μg/L, 1.46 – 89.32 μg/L and 7.45 – 87.43 μg/L respectively. In some places of Saudi Arabia, concentrations of bromate in drinking water were reported to be in the range of 3.43 – 75.04 μg/L (Table 3.8).

Table 3.8: DBPs in water distribution system

Location	Desalination Plant	DBPs	Range (μg/L)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	Reference
Dhahran, Saudi Arabia		$CHCl_3$	1.2-6.1	3.2	1.3		[38]
		BDCM	0.5-3.4	2	0.7		
		DBCM	0.0-1.2	0.5	0.3		
		$CHBr_3$	0.0-0.7	0.5	0.3		
Dhahran, Saudi Arabia		$CHCl_3$	1.26-9.3	5.51	2.18		[37]
		BDCM	0.53-1.31	0.8	0.18		
		DBCM	0.12-0.38	0.2	0.07		
		$CHBr_3$	0.1-0.24	0.12	0.03		
Red sea community, Saudi Arabia	Yanbu MSF/RO	$CHCl_3$	0.16-0.54	0.29			[173]
		BDCM	0.72-1.41	1.07			
		DBCM	1.21-2.33	1.83			
		$CHBr_3$	4.25-6.69	5.43			
Jubail	Al-jubail SWRO plant	$CHCl_3$	0.0-0.7	0.2			[174]
		BDCM	0.0-0.5	0.36			
		DBCM	0.0-1.0	0.86			
		$CHBr_3$	0.0-5.9	4.66			
Khobar	Al-Khobar MSF Plant	$CHCl_3$	0.0-0.05	0.02			
		BDCM	0.2-0.3	0.29			
		DBCM	0.9-1.1	0.99			
		$CHBr_3$	5.6-8.5	7.2			
Dammam		$CHCl_3$	0.0-0.04	0.02			
		BDCM	0.3-0.47	0.35			
		DBCM	1.0-1.9	1.4			
		$CHBr_3$	7.8-9.7	9.1			
Qatif		$CHCl_3$	0.0-0.3	0.1			
		BDCM	0.20-0.28	0.25			
		DBCM	0.7-1.22	1.07			

Location	Desalination Plant	DBPs	Range (µg/L)	Mean (µg/L)	SD (µg/L)	Median (µg/L)	Reference
		$CHBr_3$	7.7-9.7	8.54			
Rahima		$CHCl_3$					
		BDCM	0.25-0.3	0.29			
		DBCM	1.1-1.5	1.32			
		$CHBr_3$	9.0-12.0	10.67			
Khafji	Al-Khafji SWRO Plant	$CHCl_3$	0.0-0.9	0.45			
		BDCM	0.75-0.9	0.82			
		DBCM	0.86-0.92	0.9			
		$CHBr_3$	1.6-2.0	1.77			
Riyadh		$CHCl_3$	0.0-0.1	0.04			
		BDCM	0.34-0.5	0.42			
		DBCM	1.2-1.4	1.28			
		$CHBr_3$	2.3-2.7	2.42			
Dammam (Summer)	Dammam	TTHMs	0.22-26.86			9.1	
Dammam (Winter)			0.12-28.85			18.17	
Riyadh (Summer)	Riyadh	TTHMs	0.95-8.37			5.58	
Riyadh (Winter)			1.32-8.05			4.9	
Buraydah (Summer)	Buraydah	TTHMs	0.51-5.00			0.83	
Buraydah (Winter)			0.78-3.90			1.02	
Hail (Summer)	Hail	TTHMs	1.10-2.54			1.43	
Hail (Winter)			1.14-6.30			1.41	[175]
Madinah (Summer)	Madinah	TTHMs	5.37-11.00			4.57	
Madinah (Winter)			2.57-13.06			6.57	
Jeddah (Summer)	Jeddah	TTHMs	4.03-41.74			7.13	
Jeddah (Winter)			0.03-17.81			2.9	
Makkah (Summer)	Makkah	TTHMs	5.92-17.56			6.94	
Makkah (Winter)			1.39-19.29			3.17	
Abha (Summer)	Abha	TTHMs	1.43-1.88			1.52	

Location	Desalination Plant	DBPs	Range (µg/L)	Mean (µg/L)	SD (µg/L)	Median (µg/L)	Reference
Abha (Winter)			1.12-1.31			1.25	
Al-Jubail		$CHCl_3$		0.02			[176]
		BDCM		0.36			
		DBCM		0.76			
		$CHBr_3$		2.42			
Rahima		$CHCl_3$		0			
		BDCM		0.29			
		DBCM		1.32			
		$CHBr_3$		10.67			
Al-Andalus	Doha Water Blending Complex	$CHCl_3$	0.0-1.96	0.52	0.68		[172]
		BDCM	0.99-2.76	1.95	0.43		
		DBCM	2.74-7.18	4.61	1.05		
		$CHBr_3$	5.76-16.78	9.56	2.77		
Al-Jabriya, Kuwait	Doha Water Blending Complex	$CHCl_3$	0.0-2.91	0.9	0.98		
		BDCM	1.98-3.77	2.77	0.5		
		DBCM	7.0-13.73	9.19	1.5		
		$CHBr_3$	17.62-36.79	24.65	4.98		
Hawalli, Kuwait	Doha Water Blending Complex	$CHCl_3$	0.0-3.97	0.76	1.15		
		BDCM	1.27-3.78	2.22	0.57		
		DBCM	3.16-9.11	7.04	1.62		
		$CHBr_3$	12.89-33.29	24.3	4.99		
Keifan, Kuwait	Shuwaikh Water Blending Complex	$CHCl_3$	0.0-3.11	0.92	1.07		
		BDCM	1.62-7.87	2.86	1.4		
		DBCM	2.75-9.11	5.6	1.41		
		$CHBr_3$	3.38-71.52	47.43	20.87		
Al-Sharq, Kuwait	Shuwaikh Water	$CHCl_3$	0.0-5.87	0.96	1.52		
		BDCM	1.61-3.34	2.4	0.49		
		DBCM	3.02-10.25	6.72	1.54		

Location	Desalination Plant	DBPs	Range (μg/L)	Mean (μg/L)	SD (μg/L)	Median (μg/L)	Reference
	Blending Complex	$CHBr_3$	7.41-77.42	44.51	20.34		
Qatar	Ras Laffan, Ras Abu-Fontas, Ras-Girtas	$CHCl_3$	0.0-4.58	0.82			[166]
		BDCM	0.01-26.24	2.59			
		DBCM	0.01-2.43	1.04			
		$CHBr_3$	1.44-55.97	14.6			
		$CHCl_3$		0.57			[177]
		BDCM		0.32	0.08		
		DBCM		2.88	0.16		
		$CHBr_3$		3.77	0.16		
Hoora, Bahrain		$CHCl_3$		0.5			
		BDCM		0.5	0.11		
		DBCM		0.28	0.06		
		$CHBr_3$		1.28	0.11		
Salmania, Bahrain		$CHCl_3$		0.6	0.13		
		BDCM		0.73			
		DBCM		2.3	0.3		
		$CHBr_3$		3.63	0.3		
Mahooz, Bahrain		$CHCl_3$		1.2			
		BDCM		0.52	0.14		
		DBCM		0.86	0.12		
		$CHBr_3$		2.58	0.14		
Musalla, Bahrain		$CHCl_3$					
		BDCM		0.64	0.05		
		DBCM		2.4	0.1		
		$CHBr_3$		3.04	0.1		
Sanabis, Bahrain		$CHCl_3$					
		BDCM		0.73			

Location	Desalination Plant	DBPs	Range (µg/L)	Mean (µg/L)	SD (µg/L)	Median (µg/L)	Reference
		DBCM		2.4	0.1		
		$CHBr_3$		3.13	0.1		
Hammad Town, Bahrain		$CHCl_3$					
		BDCM					
		DBCM		2.9	0.1		
		$CHBr_3$		2.9	0.1		
West Riffa, Bahrain		$CHCl_3$					
		BDCM		0.46			
		DBCM		5.9	0.15		
		$CHBr_3$		6.4	0.16		
Sitra, Bahrain		$CHCl_3$		0.12	0.2		
		BDCM		0.87	0.03		
		DBCM		1.5	0.17		
		$CHBr_3$		2.49	0.17		
Umm-al, Bahrain		$CHCl_3$					
		BDCM					
		DBCM		0.27	0.1		
		$CHBr_3$		0.27	0.1		
Saudi Arabia	SWCC	Bromate	3.43-75.04				[170]
Egypt		TTHMs	7.45-87.43				[178]

3.6 DBPs Formation in Plumbing Premises

In the past studies, THMs in plumbing pipes and hot water tanks were reported to be 1.4 – 1.8 and 1.9 – 2.7 times the THMs in the water distribution system respectively [45]. THMs in the water distribution system were in the ranges of 23.0 – 26.9 μg/L, whereas it was 66.01 – 67.04 and 41.5 – 45.1 μg/L in hot water tanks and plumbing pipes respectively [45]. In all sampling locations, THMs in the plumbing pipes were 136 – 181% of the THMs in the water distribution systems [45]. In a recent study in Dhahran, Saudi Arabia, THMs in hot water tanks and plumbing pipes were detected to be 1.6 – 3.0 and 1.1 – 2.4 times, respectively, to THMs in the water distribution networks, while HAAs were 0.9 – 1.8 and 1.2 – 1.9 times, respectively, to HAAs in the water distribution networks. The chronic daily intakes of DBPs from plumbing pipes and hot water tanks were 0.6 – 1.8 and 0.5 – 2.3 times to the intakes from water distribution networks [23]. This study reported that the cancer risks from plumbing pipes and hot water tanks were 1.46 (0.40 – 4.3) and 1.68 (0.35 – 5.1) times to the cancer risks from water distribution networks [23].

CHAPTER 4

METHODOLOGY

This chapter describes the data collection methods and models for predicting human exposure and risk. The first and second segment of this chapter define data collection and experimental methods of desalinated and blended water samples. The third and fourth part describe the systematic scenarios and models for predicting human exposure and risk from trihalomethanes present in desalinated and blended water.

4.1 Data Collection

Occurrences of THMs (chloroform: $CHCl_3$; bromodichloromethane: BDCM; dibromochloromethane: DBCM; and bromoform: $CHBr_3$) and water quality parameters were investigated in desalinated seawater and blended water (mixture of desalinated seawater and treated groundwater in the ratio of 40 – 60%) in the WDS in Al-Khobar and Dhahran, Saudi Arabia for a period of one year (Feb, 2014 – Jan 2015). The samples were collected on a bi-weekly basis. Approximately 24 samples were collected from each location. Additional 3 samples were collected from each location for confirmatory purposes. Samples for measuring THMs were collected in 100 mL glass vials containing the dechlorinating agent of 100 mg/L (e.g., ammonium chloride) and the samples for other parameters (e.g., pH, temperature, UV_{254}, DOC, etc.) were collected in 125 mL plastic bottles. The samples were transported to the laboratory in a cooler (< 4ºC).

4.2 Sample Analysis

Temperature and pH were measured *in-situ*. The free residual chlorine (FRC) and total chlorine (TC) were measured by HACH spectrophotometer (HACH DR 3900 model) following HACH methods 8021 and 8167 respectively. Turbidity was measured with a turbid meter (HACH model 2100N). Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured with the Shimadzu TOC analyzer (Model: TOC-L-CSN) following standard method 5310B [179]. The ultraviolet absorption (UV_{254}) was measured using a spectrophotometer (Genesys 10 UV VIS model) at 254 nm with a 10 mm optical path quartz cell. Prior to measuring DOC and UV_{254}, samples were filtered through 0.45 µm membrane filters. THMs were measured by gas chromatography equipped with mass spectroscopy detector (GC–MS) (Varian chromatograph, model 3900 equipped with quadruple mass spectrometer). The analysis was conducted according to the USEPA method 551.1 [180,181].

4.2.1 Measurement of THMs

The determination of THMs in water samples was accomplished by liquid-liquid extraction and gas chromatography with micro electron capture detection according to the USEPA method 551.1 [180,181] in the laboratory of the Department of Chemistry of King Fahd University of Petroleum and Minerals and Al-Hoty Commercial Laboratory, Al-Khobar, Saudi Arabia. Ammonium chloride and phosphate buffer were added to preserve the sample. Ammonium chloride was used to convert the free chlorine into monochloramine and phosphate buffer was used to lower the sample pH to 4.8 to 5.5. The preserved samples were taken from the storage and allowed to equilibrate to room temperature. Six µL of the

surrogate analyte fortification solution (125,000 μg/L 1, 2, 3-trichloropropane in acetone) was injected into 30 mL of sample and mixed carefully by inverting the sample vial two times with minimal sample agitation. Exactly 3.0 mL of methyl tertiary butyl ether (MTBE) was added to the sample. Eight grams of NaCl was added and sample vial was shaken vigorously and consistently by an orbital mixer for thirty seconds. The vial was inverted to allow the separation of water and MTBE phases (approx. fifteen minutes). Using a graduate disposable pipet, 2 ml of the top organic layer of the solvent phase was transferred to an auto sampler vial. Standard samples and blank samples were prepared for calibration according to the same procedure. For standard samples, 10 ppb, 25 ppb, 50 ppb, 75 ppb and 100 ppb of total trihalomethanes (TTHM) were used, and for blank samples, distilled water was used. Trihalomethanes were identified and measured by capillary column gas chromatography using Varian chromatograph, model 3900 equipped with a quadruple mass spectrometer. Using the standard samples, a calibration curve was drawn. Total ion count for 100 ppb THMs and a sample is shown in Figure 4.1 and 4.2 respectively. The calibration curve of dibromochloromethane (DBCM) is shown in Figure 4.3. Using the total ion count in the calibration curve, concentrations of trihalomethanes were measured.

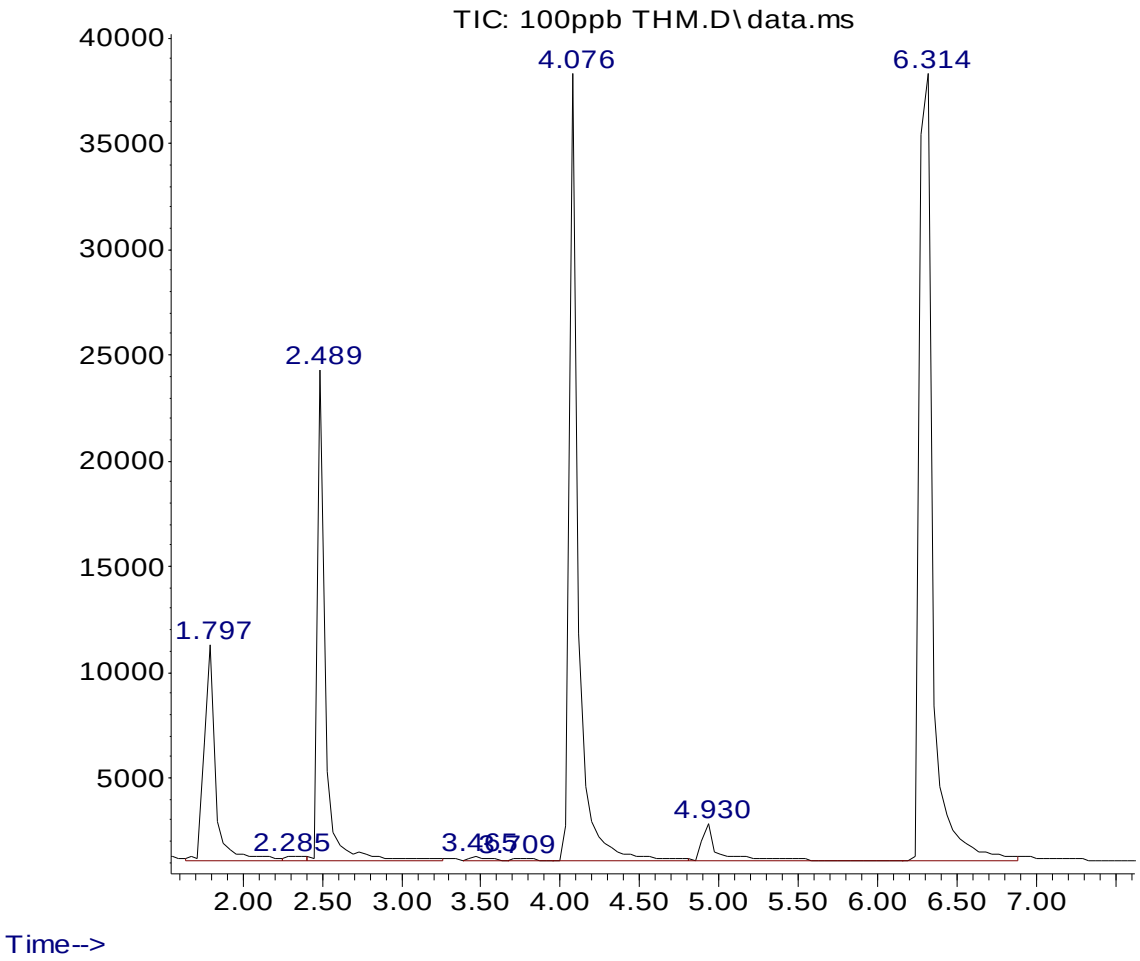


Figure 4.1: Total ion count (TIC) of 100 ppb TTHMs in a scan mode

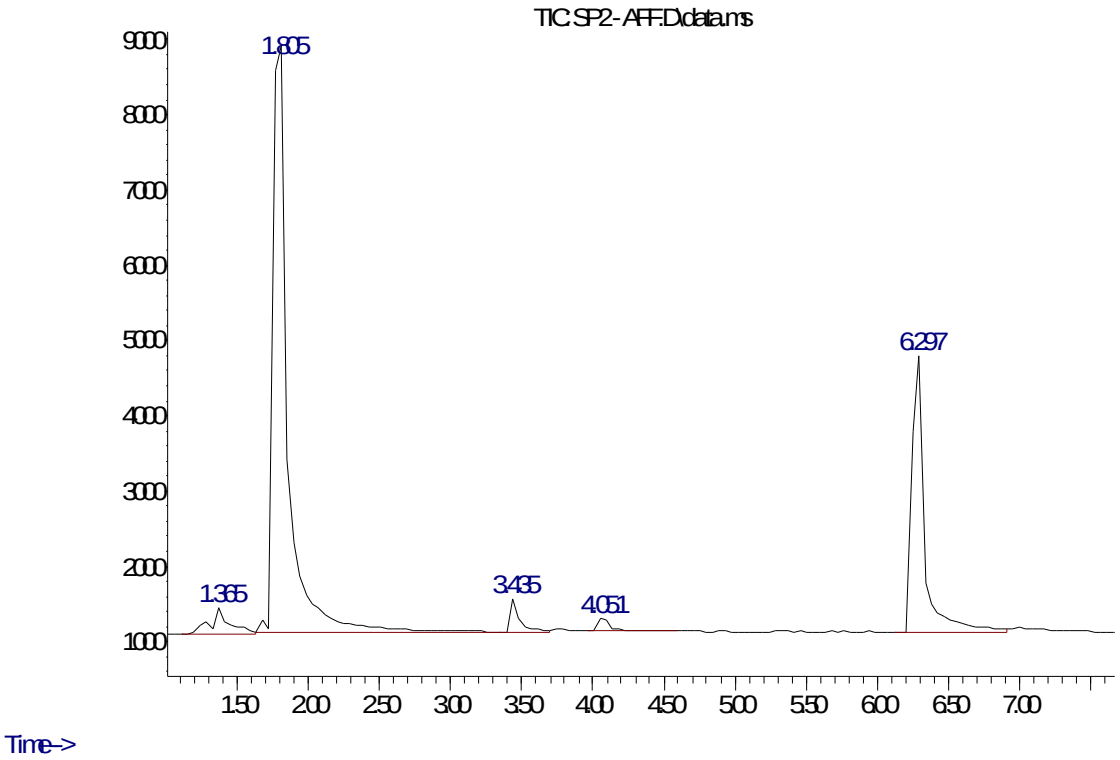


Figure 4.2: Sample Set 2: Example of Total Ion Count (TIC) in a SCAN mode of Tap 3, SP-B-3 on February 2014

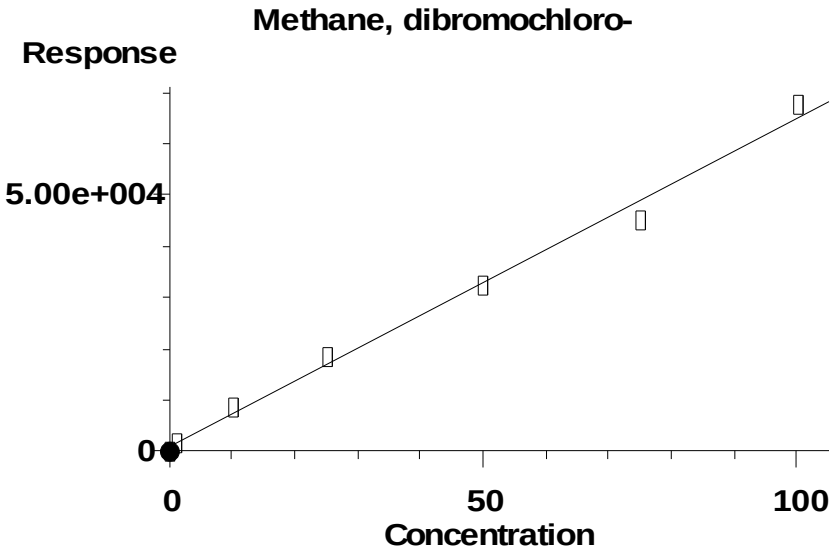


Figure 4.3: Calibration curve for BDCM

4.3 Data Analysis

The data were analyzed using the statistical software (JMP™ and Minitab™) and are presented through summary tables and boxplots. The outliers were identified through boxplots. The experimental data obtained in this study were fused into the available data in the literature and the regional variability of different THM compounds in the desalinated and blended water were analyzed. The analyses were also performed with respect to the type of source water (e.g., Red Sea and Arabian Gulf), blended water, desalination process and geographical locations. The data were further analyzed to identify the best-fit statistical distributions.

4.4 Risk Assessment

The 1st step of risk assessment is to identify the chemicals that pose risk to human, which is followed by the identification of various routes of exposure and potential exposed human population. The third step is a combination of assessing exposure scenarios and dose-response relationship. Exposure assessment is done by quantifying contaminant dose over the lifetime, also known as the chronic daily intake (CDI). The relation between dose and response is established by compiling toxicological profiles and evaluating toxicity indices. Toxicity indices are developed using the animal bioassay data, which is transformed into slope factor (SF: 95 percentile upper bound probability of an individual having cancer from lifetime exposure to a carcinogen) and reference dose (R_fD: maximum level of a chemical that can be ingested safely) for human cancer and non-cancer risks respectively. In the 4th step, the CDI and SF and/or R_fD are used to predict human cancer and non-cancer risks through multiple routes of exposure (e.g., ingestion, inhalation and dermal pathways). The following step is the risk management, in which various alternatives are evaluated to determine the best action to reduce risk. The last step is communicating with regulatory bodies to assist in achieving maximum benefit for minimum cost. Figure 4.4 shows a schematic diagram of basic risk assessment framework.

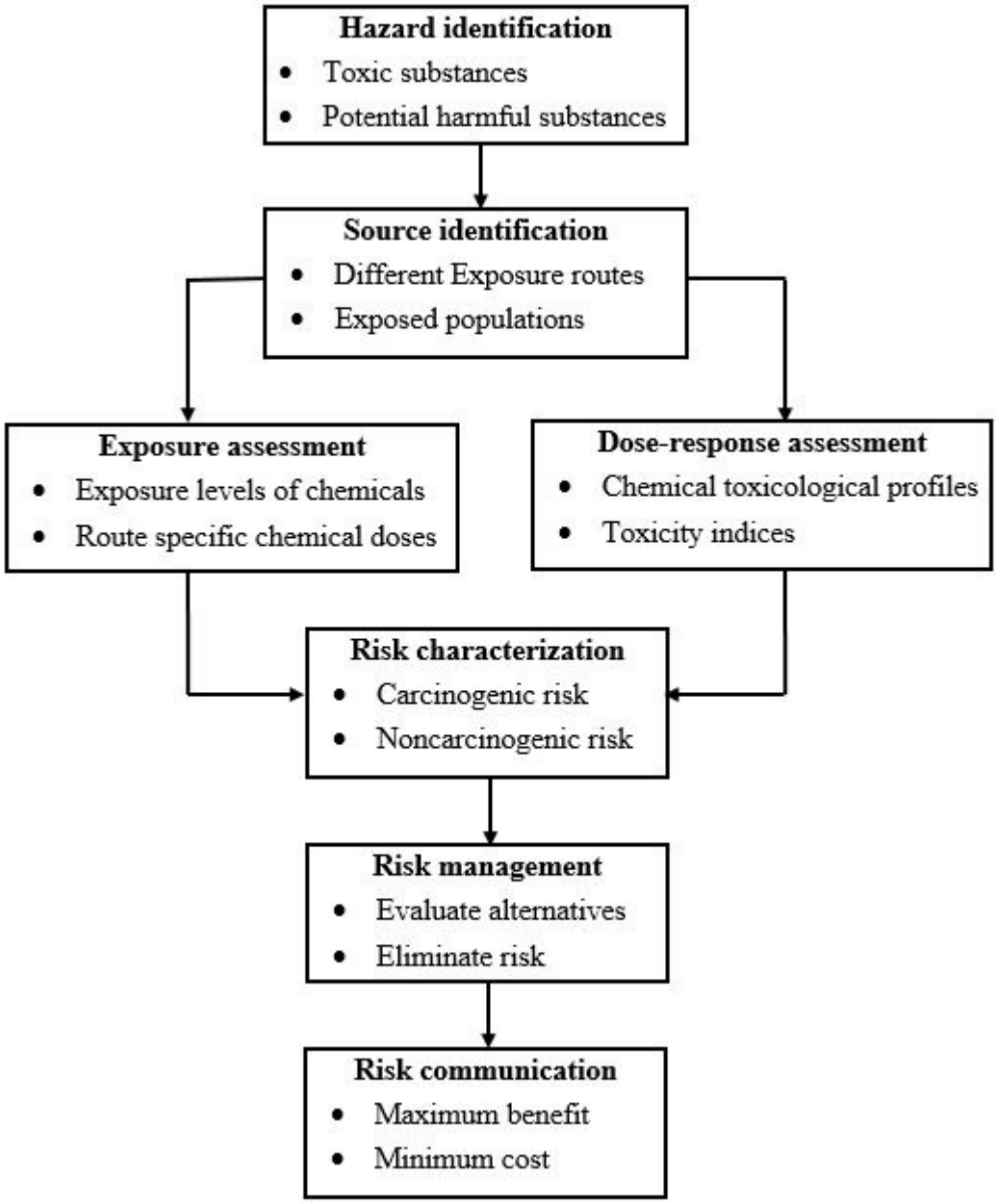


Figure 4.4: Risk assessment framework

4.4.1 Hazard Identification

The chlorinated byproducts, known as DBPs, have been an active area of research to ensure the safe drinking water to the community. To date, over 100 types of DBPs have been identified, which could form only a fraction of the entire spectrum of DBPs in municipal water [76]. Research to date has demonstrated that the municipal water can be a potential source of DBPs. In different stages of water processing, DBPs can be formed in municipal water while the type and quantity of disinfectant and other physical and operational parameters (e.g., pH, temperature, etc.) can play an important role. Although a large number of DBPs have been reported in municipal water to date, only a few of those are currently regulated by several agencies. In recognition of the concern of DBPs, concentrations of few DBPs (e.g., THM_4, HAA_5, Bromate, etc.) are regulated by several organizations. In this study, only THMs in desalinated and blended water were considered. Table 3.7 and Table 3.8 in Chapter 3 show the potential occurrences of THMs. Table 2.8 in Chapter 2 demonstrates that the lifetime exposure to THMs from municipal water might pose elevated cancer and non-cancer risks to humans.

4.4.2 Exposure Assessment

Exposure to THMs can be occurred through multiple pathways, including ingestion of drinking water, and inhalation and dermal contact during showering, bathing, house cleaning and swimming [182,183]. Exposure assessment is associated with uncertainty from different sources, including rate of water ingestion, life expectancy, temperature of cold and hot water, mixing ratio of cold and hot water, free residual chlorine, DBPs formation kinetics, characteristics and quantities of natural organic matter (NOM), shower

stall volume, water flow, dermal absorption coefficients and shower duration [39,182]. Obtaining precise data for these parameters is a challenge. To incorporate uncertainties, 5000 random data are generated for each parameter following their statistical distributions. Exposure to THMs through ingestion is predicted using the THMs in cold water. THMs exposure through inhalation pathway is predicted using THMs in the shower air, which is estimated using the partition coefficients and mass-balance equations. In assessing dermal exposure during showering events are divided into the unsteady and steady states and exposure is predicted for both stages separately. Further details are summarized below.

4.4.2.1 Ingestion Pathway

The Chronic daily intake (CDI) of THMs through ingestion of drinking water is computed according to the method specified by USEPA as [35,38,184,185]:

$$CDI_{ing} = \frac{C_w \times EF \times IR \times ED \times CF}{BW \times AT} \quad (4.1)$$

Where, CDI_{ing} = chronic daily intake via ingestion (mg/kg-day); AT = averaging time (days); BW = weight of the body (kg); C_w = concentration of THMs in drinking water (μg/L); ED = exposure duration (year); EF = exposure frequency (days/year); IR = rate of drinking water ingestion (L/day); and CF = mass conversion factor from μg to mg (0.001).

4.4.2.2 Inhalation Pathway

The CDI of THMs through inhalation pathway can be predicted as [35,38,184,185]:

$$CDI_{inh} = \frac{E_r \times C_a \times t \times R \times F \times EF \times ED \times CF}{BW \times AT} \quad (4.2)$$

Where, CDI_{inh} = chronic daily intake of THMs via inhalation (mg/kg-day); AT = averaging time (days); BW = weight of the body (kg); C_a = concentrations of THM in shower air ($\mu g/m^3$); ED = exposure duration (year); EF = exposure frequency(days/year); E_r= THMs absorption efficiency through respiratory apparatus; F = shower frequency (shower/day); R = rate of breathing (m^3/min); t = duration of shower (min/shower); and CF = mass conversion factor from μg to mg (0.001).

C_a is the concentrations of THMs in shower air, which depends on various factors including water flow rate of shower, shower stall volume, THMs concentrations in cold water, mass transfer rate, duration of shower and shower air exchange rate. C_a can be modeled as [38]:

$$\frac{dC_a}{dt} = \frac{1}{V}(Q_w p_v C_w - k_a V C_a) \qquad (4.3)$$

Where, C_a = THMs concentration in the compartment ($\mu g/m^3$); V = Shower stall volume (m^3); k_a = air exchange rate in shower stall (min^{-1}); Q_w = water flow (L/min); p_v = THMs transfer efficiency from water to air; and C_w = concentration of THMs in cold water.

THMs concentration in air is assumed to be zero during the pre-exposure period because the shower air had insignificant THMs concentrations prior to this event. So, the boundary conditions $C_a|_{t=0}=0$ is introduced and equation 4.3 is solved for $C_a|_{t=t}$ as [38]:

$$C_a(t) = \frac{Q_w p_v C_w}{k_a V}(1 - e^{-k_a t}) \qquad (4.4)$$

In equation 4.4, THMs in shower water is required to estimate inhalation of THMs in during showering. During showering, the temperature of the water is in the range of 35-45^0C, as hot water and cold water are generally mixed. THMs increase at a higher rate in

hot water than that of a cold water due to temperature-driven reaction rate. However, prediction of THMs increase in the mixed water during showering requires information on the baseline concentrations of THMs in hot and cold waters coming through the tap, their mixing proportions, residual chlorine, residual organics and temperature of the mixed water [39]. As such, concentrations of THMs are generally not constant over the showering period [38]. THMs growth rate can be predicted by using the following equations in the shower water[38]:

$$k = 0.0011e^{0.0407T} \quad (4.5)$$

Where, T = temperature of water (°C); and k = THM growth rate at T °C (min^{-1}). Using the above equation, THMs in the heated water during the shower time can be predicted as [38]:

$$C_{hw} = C_w e^{(k_1 - k_2)t} \quad (4.6)$$

Where, C_{hw} = THM concentrations in heated water (µg/L); C_w =THM concentrations in cold water (µg/L); k_1 = THM formation rate for heated water (min^{-1}), k_2 = THM formation rate for cold water (min^{-1}) which can be estimated using Eq. (4.5); and t = shower duration (min). Using C_{hw} instead of C_w in Eq. (4.4), the shower air concentrations (C_a) is estimated. THM concentrations in the air within the shower stall (C_a) are used in Eq. (4.2) to predict chronic daily intakes through inhalation (CDI_{inh}).

4.4.2.3 Dermal Contact

THMs can be absorbed through the human skin during showering. . Figure 4.5 shows the cross section of human skin, which shows different layers of skin.

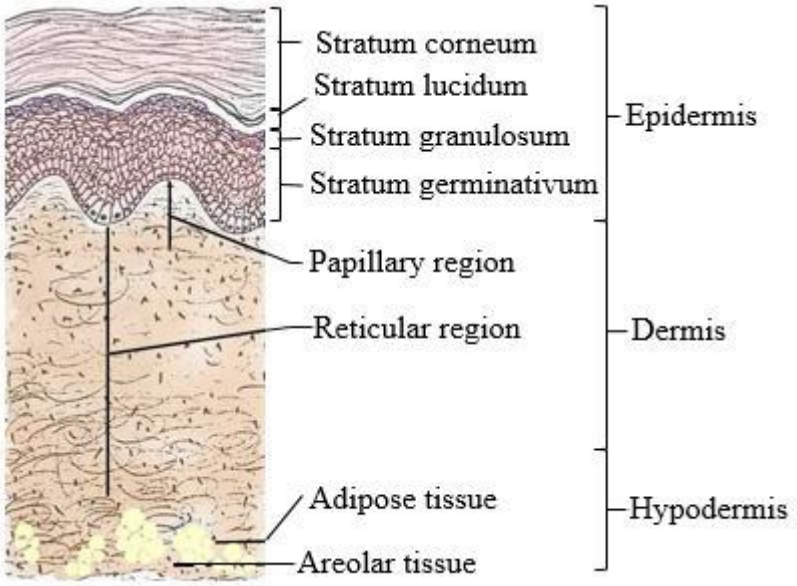


Figure 4.5: Cross section of skin (modified after [186,187])

Human skin is a complex organ, which has multiple layers: the outside layer, known as the stratum corneum and the innermost layer, known as the dermis. The stratum corneum acts as a barrier to chemical intrusion through the skin. The chronic daily intakes (CDI) through dermal route depend on the thickness of stratum corneum, molecular diffusion of a chemical through stratum corneum, partition coefficient between stratum corneum and chemical in the water and the concentration gradient between the upper and lower layers of stratum corneum [38]. Depending on the shower duration, the chemicals in water attached to the outside of human skin may follow the unsteady state or both the unsteady and steady states of exposure. As such, dermal absorption of THMs might be significantly different depending on the states of exposure (e.g., unsteady vs. steady states). Consequently, unsteady or both unsteady and steady state analysis may be required. The past studies reported that the steady state diffusion coefficient through the stratum corneum

was in the order of 10^{-13} to 10^{-14} m^2/s for compounds having low molecular weight (<500 Da) and 10^{-15} to 10^{-17} m^2/s for compounds having high molecular weight (e.g. albumin, polystyrene) [188,189]. The diffusion of chemicals before reaching the steady state condition can be significantly different from the steady state values [190]. To achieve the steady state condition between the stratum corneum and the DBPs layer on the skin surface, DBPs require a time, which is known as the lag time. The lag time for the typical DBPs in municipal water was reported to be in the range of 9.8 to 391.2 minutes [38]. The lag time (L_t) prior to achieving steady state condition between the skin exposed and substances in the water can be estimated as [38,190]:

$$L_t = \frac{d_{skin}^2}{6 \times D_{skin}} \tag{4.7}$$

Where, L_t = lag time (h); d_{skin} = thickness of stratum corneum (cm); D_{skin} = molecular diffusion of chemical through stratum corneum (cm^2/h). The molecular diffusion (D_{skin}) is estimated as [38]:

$$D_{skin} = MW^{-0.6}\left(\frac{2.4 \times 10^{-6} + 3 \times 10^{-5} K_{ow}^{0.8}}{K_m}\right) \tag{4.8}$$

Where, MW = molecular weight of chemical (g/mol); K_{ow} = octanol–water partition coefficient; K_m = partition coefficient between stratum corneum and chemical in the water. K_m can be estimated as [38]:

$$K_m = 0.64 + 0.25\, K_{ow}^{0.8} \tag{4.9}$$

Using Fick's first law of diffusion, the influx of THMs through stratum corneum (J) can be predicted as [38]:

$$J = \frac{D_{skin} \times \Delta C}{d_{skin}} \quad (4.10)$$

Where, J = diffusion through human skin (mg/m^2/h); d_{skin} = thickness of stratum corneum (m); D_{skin} = molecular diffusion of the chemical through stratum corneum (m^2/h); and ΔC = concentration gradient between the upper and lower layers of stratum corneum (μg/L). The equation (4.10) can be modified by incorporating equation (5) and (6) to predict the influx of THMs through stratum corneum (J) as [38]:

$$J = \frac{D_{skin} \times \Delta C_w e^{(k_1 - k_2)t}}{d_{skin}} \quad (4.11)$$

The concentration gradient between the upper and lower level of stratum corneum do not follow a linear pattern [38]. Chowdhury [38] used one-minute intervals to characterize the non-linear pattern. The equation (4.11) becomes

$$J_i = \frac{D_{skin} \times \Delta C_w e^{(k_1 - k_2)t_i}}{d_{skin}} \quad (4.12)$$

$$J = \sum_{i=1}^{n} J_i \quad (4.13)$$

Where, i = 1, 2, 3,….., n; and the time unit is t/n.

In the unsteady state condition during showering, the CDI via dermal pathway can be estimated as [38]:

$$CDI_{derm-ust} = \frac{J \times S_{skin} \times t \times F \times EF \times ED \times CF}{BW \times AT} \quad (4.14)$$

Where, $CDI_{derm-ust}$= chronic daily intake of THMs through dermal contact during the unsteady-state condition (mg/kg-day); J = diffusion through human skin (mg/cm^2/min); S_{skin} = body skin area exposed to water (m^2); t = duration of shower per event (min/event); F = frequency of shower (event/day); EF = exposure frequency (day/year); ED = duration of exposure (year); BW = weight of the human body (kg); AT = averaging time (day); CF = 10,000 (conversion factor for skin area from m^2 to cm^2).

After lag time, steady state condition is achieved, in the cases where showering duration is more than the lag time, dermal exposure for the steady-state period can be estimated as [38]:

$$CDI_{derm-ss} = \frac{C_{hw} \times S_{skin} \times P_d \times t_{ss} \times EF \times F \times ED}{BW \times AT} \quad (4.15)$$

Where, $CDI_{derm-ss}$ = chronic daily intake of THMs through dermal contact (mg/kg-day) during steady-state; C_{hw} = THM concentrations in warm water (µg/L); S_{skin} = area of body skin exposed to water (m^2); P_d = permeability of THMs through the skin (m/min); t_{ss} = difference between showering duration and lag time (min/event). The CDI of THMs through dermal contact pathway is calculated as the sum of chronic daily intakes during the unsteady and steady state conditions as:

$$CDI_{derm} = CDI_{derm-ust} + CDI_{derm-ss} \quad (4.16)$$

Upon estimation of route specific CDI, the lifetime cancer and non-cancer risks from exposure to THMs can be estimated as:

$$CR = \sum_{i=1}^{m}\sum_{j=1}^{n} CDI_{ij} \times SF_{ij} \quad (4.17)$$

$$HI = \sum_{i=1}^{m} \frac{CDI_i}{R_fD} \quad (4.18)$$

Where, *i = 1,2,3,4…m* representing different THMs (i.e. $CHCl_3$, BDCM, DBCM and $CHBr_3$); *j = 1,2,3,4…n* representing different routes of exposure (i.e. ingestion, inhalation and dermal contact); CR = cancer risk; SF = slope factor ($[mg/kg/day]^{-1}$) for specific route; R_fD = reference dose (mg/kg/day). The CDI will be estimated through generating 5000 random data using the parameter values and the statistical distributions.

In exposure analysis, a number of parameters are required in addition to the concentrations of THMs in water. The values of these parameters were obtained from the literature. A brief summary of their values are provided below:

- The parameters for exposure analysis other than the concentrations of THMs are many, including: water ingestion rate, body weight, air intake rate, area of body skin exposed to water during showering, permeability of THMs through skin, molecular weight of THMs, octanol-water partition coefficient of THMs, exposure frequency, exposure duration, averaging time, water flow of shower, shower stall volume, shower duration, water temperature, air change rate of shower stall, shower frequency, absorbance capacity of THMs through human respiratory system, water to air phase transformation rate of THMs and thickness of stratum corneum of skin etc. Most of the parameters are associated with uncertainty. In incorporate the

uncertainty, triangular distributions are used. The values of the parameters for statistical distributions are shown in Table 5.4.

- Body weight, water ingestion rate, air intake rate, the area of body skin exposed to water during showering vary for different age groups. The values of the above parameters are taken for three different age groups: <2 years, 2-16 years and >16 years age group. The separation of age groups assists in addressing the early life exposure scenarios. The values for these parameters are taken from exposure factors handbook [191], which is based on Continuing Survey of Food Intakes by Individuals (CSFII) and National Health and Nutrition Examination Survey (NHANES) data. The data have received a high level of peer review and the confidence on these data are medium to high [191,192]. The distributions of these parameters are assumed to be triangular. The 10^{th} percentile value is taken as the minimum value, 50^{th} percentile value is taken as mode and 90^{th} percentile value is taken as the maximum value. For example, the water ingestion rate for the age group follows the triangular distribution with the minimum value of 0.74 L/day, the most likely value of 1.31 L/day, and the maximum value of 2.12 L/day.

- The values of exposure duration, frequency, averaging time and shower frequency are taken from exposure factor handbook [191].

- Exposure durations were considered to be the lifetime due to continuous dependence on water. However, it was assumed that a person on average may be exposed to the supply water for 350 days out of 365 days, due mainly to travel to

other places. Exclusion of two weeks has also been recommended by the USEPA [191].

- Other parameter values related to THMs are taken from various research articles on disinfection byproducts [39,182,193].

4.4.3 Dose-Response Modeling

The risk potentials of the chemicals are estimated following the dose-response models. Typically, the target chemicals are applied to a group of animals (mostly, mice) by varying the doses for certain period under control environment and the corresponding effects are measured. The animal bioassay data are transferred to human risk potentials following several models [128]. The toxicity data (Reference dose, slope factor) for THMs were obtained from USEPA (2016), and are shown in Table 2.8 in Chapter 2. Further details on dose-response model can be obtained in the literature [176,184–186].

4.4.4 Adjustment Factor

According to USEPA [184], the early-life exposure has a higher contribution to cancers appearing later in life. To represent such an effect, age-dependent adjustment factors (ADAF) are used to slope factor suggested by USEPA [184]:

- An increase of 10-fold to slope factor for exposures up to 2 years of age from birth;
- An increase of 3-fold to slope factor for exposures between 2 years to less than16 years of age; and
- No adjustment after turning 16 years of age.

In this study, similar adjustments were incorporated in risk assessment.

4.4.5 Estimating Disability Adjusted Life Year (DALY)

For priority setting and implementation purposes, quantifying the burden of diseases or injuries and determining the relative characteristics of risk factors to the burden are very important for policy makers. To address this issue, the concept about burden of disease t was introduced by WHO in 1996 [194]. The global burden of disease (GBD) study estimated the total burden of disease throughout the world as the summation of the burden of all diseases. To represent the burden of a disease, the total amount of health loss at the population level due to the disease is calculated in terms of disability adjusted life years (DALY) [194]. The DALY is a time-based concept that combines years of life lost due to premature mortality and disability caused by a disease or injury [194]. It combines the lost years due to premature mortality (years of life lost), known as YLL and healthy life lost while living with a disability (years lived with disability), known as YLD. To assess YLD, disability weight (DW) is an essential parameter. DW is given to someone living with disability, anchored between 0 and 1, to reflect the impact of a specific health condition [195]. Initially, Murray et al. [194] examined over 100 specific diseases with a disability component to obtain a large set of DWs. It was derived from the terminology of the International Classification of Diseases (ICD) [195]. The GBD disability weights are currently used to measure the burden of diseases in terms of DALY [196]. However, the GBD approach may underestimate the burden of injury and specific external causes by ignoring temporary consequences of injuries or diseases and therefore, may affect prioritization of resources for disease or injury prevention [195]. But, it fairly shows the long-term health consequences in terms of DALY and quantifies the burden of disease that can be used for cost-effective analysis to assist international health policy [197].

In this study, DALY is estimated for the possible effects of exposure to disinfection byproduct (DBPs). A number of organs may be susceptible to cancer from exposure to DBPs in municipal water [198,199]. Previous epidemiological studies have shown that some cancer risks might be associated with the DBPs in drinking water [198,199]. In particular, exposure to DBPs may elevate the bladder cancer, which was demonstrated in few previous studies [198,199]. To assess the DALY for bladder cancer, three possible cases are considered:

i. A proportion of diseased people will die from bladder cancer;

ii. A proportion of them will be cured of this cancer; and

iii. Rest of them will live with the cancer sequelaes.

The healthy years of life lost in a population is calculated as [200]:

$$DALY = YLL + YLD \tag{4.19}$$

YLL is the total years of life lost due to premature mortality for cancer, which accounts for the case (i) and YLD is the total years lived with disability, which accounts the cases (ii) and (iii). The YLL and YLD are calculated as [200]:

$$YLL = \sum_{x} n_x d_x e_x \tag{4.20}$$

$$YLD = \sum_{x,y} n_x i_{x,y} DW_y L_y \tag{4.21}$$

Where, YLL = the years of life lost due to premature mortality, YLD = the years of life lost due to disability caused by disease, n = numbers of population, d = death rate of population; i = incidence rate, DW = adjusted disability weight, L = duration of disability,

x = age group, y = disease phase and e = standard life expectancy. The widely used models [201] to estimate the YLL and YLD using age-specific cancer incidence (P_x) and survival rate (S_x) are followed in this study. These models can be expressed as [201]:

$$YLL = \sum_{x} n_x P_x (1 - S_x)(e_x - T_D) \tag{4.22}$$

$$YLD = \sum_{x} n_x P_x [(1 - S_x)DW_y L_y + S_x\{DW_y L_y + P_{seq} DW_{seq}(e_x - T_c)\}] \tag{4.23}$$

Where, P_x = age - specific lifetime cancer estimate. The lifetime cancer risk is converted into age-specific cancer estimate. However, there are differences in probabilities of developing cancer at different age groups. To account these uncertainties, a parameter known as the age-specific relative sensitivity (RS_x) is introduced; this is calculated as the ratio of age-specific incidence rate of bladder cancer to the total incidence rate in the population [201,202].

$$RS_x = \frac{I_x}{I} \tag{4.24}$$

Where, I_x = bladder cancer incidence rate for each age group, I = total bladder cancer incidence rate for the total population. The incidence rate is based on the estimates available in GLOBOCAN database [203]. The GLOBOCAN is an online database for cancer, developed by the International Agency for Research on Cancer (IARC), which is a sister organization of World Health Organization (WHO). The age-specific cancer rate is calculated as:

$$P_x = \frac{CR \times RS_x}{Sp_x} \tag{4.25}$$

Where, CR = probability of an individual developing cancer (cancer risk); RS_x = age-specific relative sensitivity; and Sp_x = age span. S_x is the survival rate, which is estimated for each age group. A good approximation of survival rate is the complement of the ratio of cancer mortality to cancer incidence rate, which is expressed as [204]:

$$S_x = 1 - \frac{M_x}{I_x} \tag{4.26}$$

Where, M_x = cancer mortality rate for each age group, I_x = cancer incidence rate for each age group, based on the GLOBOCAN estimate [203].

e_x = standard life expectancy taken from Global Burden of Disease Studies (GBDS) [194].

L = duration of disability. It is divided into three phases: times for diagnosis and treatment (L_D), times for pre-terminal phase (L_M) and times for terminal phase (L_T), which is set as 4 months, 3 months and 1 month, respectively [200].

T_D = the median time to death taken as 2.20 years for bladder cancer following the available cancer registry [205].

T_c = the median time to cure taken as 4 years for bladder cancer reported by the same cancer registry [205].

DW = adjusted disability weight ranging from 0.0 to 1.0 taken from GBDS [194].

P_{seq} = proportion of the sequelae [205–207].

DW_{seq} = disability weight of sequelae [205–207].

CHAPTER 5

RESULTS AND DISCUSSION

Chapter five is divided into four parts. The first part describes the data of trihalomethanes in the desalinated and blended water. The second part describes the estimated chronic daily intake, cancer and non-cancer risk and financial burden from exposure to trihalomethanes. In the third part, a methodology is proposed to control risk from the exposure to trihalomethanes. Lastly, there is a discussion based on the results.

5.1 Data

Concentrations of THMs and water quality parameters for the desalinated and blended water are shown in Table 5.1. The blended water had higher level of organic matter (e.g., DOC, UV_{254}) than the desalinated water (Table 5.1). Concentrations of THMs in blended water were significantly higher than that in the desalinated water (Table 5.1). In this study, average concentrations of THMs in the desalinated and blended waters were 10.08 and 19.2 µg/L respectively with the ranges of 0.1 – 33.6 and 2.1 – 52.4 µg/L respectively (Table 5.1).

Table 5.1: Summary of water quality parameters and THMs in desalinated and blended water

	Desalinated water		Blended water	
	Average	Range	Average	Range
DOC (mg/L)	0.78 (0.33)	0.39–1.68	1.98 (0.41)	1.27–3.14
TC (mg/L)	0.55 (0.09)	0.33–0.72	1.1 (0.23)	0.69–1.54
FRC (mg/L)	0.44 (0.16)	0.24–0.72	0.82 (0.23)	0.07–1.29
Bromide (mg/L)	0.28 (0.13)	0.10–0.64	0.30 (0.21)	0.18–0.76
Water temperature (°C)	26.3 (5.8)	20–39	25.4 (6.4)	19–37
pH	6.9 (0.49)	6.6–7.7	7.13 (0.12)	6.7 – 8.1
Turbidity (NTU)	0.21 (0.09)	0.13–0.38	0.33 (0.15)	0.14–0.46
UV_{254} (/cm)	0.015 (0.01)	0.01–0.04	0.04 (0.01)	0.02–0.058
Conductivity (µS/cm)	230.4 (43.9)	149-348.7	415.3 (72.4)	266.4-552.5
THMs (µg/L)	10.08 (2.1)	0.1-33.6	19.2 (4.7)	2.1-52.4

DOC: Dissolved organic matter; TC: total chlorine; FRC: Free residual chlorine; Values within brackets are standard deviations.

Concentrations of THMs in desalinated and blended water from few other plants in Saudi Arabia, and some Arabian Gulf countries are summarized in Table 5.2 [17,20,38,154,165,166,169,172–177,208]. In the major cities of Saudi Arabia, THMs in desalinated water were in the range of 0.1 – 41.7 µg/L [175]. In blended water, THMs were in the ranges of 0.1 – 66.7 µg/L [17,20]. THMs in blended water were higher than the desalinated water, due mainly to extended reaction period, higher free residual chlorine and higher levels of NOM in blended water [39,209]. THMs in desalinated water from the Eastern and Western regions of Saudi Arabia were in the ranges of 0.12 – 28.85 and 4.03 – 41.74 µg/L respectively [175]. The sources of water for the eastern and western regions

were the Arabian Gulf and the Red Sea respectively. The RO plants generally had higher THMs than the thermal plants. THMs from the RO and thermal plants were in the ranges of 0.1 – 30.12 and 0.1 – 10.97 µg/L respectively [17,165,173,174,176]. For an example, Jeddah plant is an RO process, which had THMs in the range of 6.25 – 30.12 µg/L with an average of 9.47 µg/L [154]. In a thermal process in Al-Khobar, THMs were in the range of 3.70 – 9.95 µg/L with an average of 6.08 µg/L [174].

Table 5.2: Concentration of THMs in desalinated and blended water in the Gulf countries[1]

Country	THMs	Average	Std. Dev.	Min	Max	Reference
Saudi Arabia	$CHCl_3$	0.71		0	9.3	[8,22,58-69]
	BDCM	0.86		0	7.87	
	DBCM	1.46		0	13.33	
	$CHBr_3$	15.74		0	62.42	
Qatar	$CHCl_3$	0.6		0.01	4.96	[166]
	BDCM	0.21		0.01	2.66	
	DBCM	0.52		0.01	2.74	
	$CHBr_3$	20.89	15.2	3.99	72.95	
Kuwait	$CHCl_3$	0.81	1.13	0	5.87	[172]
	BDCM	2.44	0.84	0.99	7.97	
	DBCM	6.63	2.11	2.74	13.73	
	$CHBr_3$	30.16	19.6	3.38	77.42	
Bahrain	$CHCl_3$					[177]
	BDCM	0.6	0.12			
	DBCM	0.64	0.05			
	$CHBr_3$	5.9	0.15			

[1]Concentration are given in µg/L in the table

Concentrations of THMs in the desalinated and blended water in Kuwait and Qatar were reported to be higher (Table 5.2). THMs in the desalinated and blended water from Bahrain, Kuwait, Qatar and UAE were reported to be in the ranges of 0.27 – 6.4, 7.11 – 104.89, 4.02 – 83.31 and 7.0 – 15.0 µg/L respectively (Table 5.2), with the averages of 2.95, 40.04, 22.22 and 10.0 µg/L respectively [20,155,166,172,177]. Among the THMs, concentrations of brominated THMs were much higher than the chlorinated ones. The higher fractions of brominated THMs were due to higher levels of bromide in the desalinated seawater [17,20]. Past studies have reported the concentrations of bromide in seawater in the range of 50,000 – 80,000 µg/L and in desalinated seawater it ranged from 250 to 600 µg/L [13,14,18,20,21]. Recent studies showed that the levels of bromide in desalinated and blended water in Saudi Arabia were in the range of 70 – 670 µg/L with an average of 340 µg/L [210]. The higher fractions of brominated THMs can be a concern to human health because of their higher toxicity than $CHCl_3$, and the brominated THMs are possible/probable human carcinogens [184]. The THMs database obtained through this study was expanded using the additional data from the desalinated and blended waters in different desalination plants and WDS in the major cities in Saudi Arabia [17,20,38,154,165,166,169,172–177,208]. The additional data from multiple desalination plants and cities have explained data variability among different plants and cities, and thus the data variability was incorporated to better explain human exposure and risk. In Saudi Arabia, average concentrations of $CHCl_3$, BDCM, DBCM and $CHBr_3$ were 0.71, 0.86, 1.46 and 15.74 µg/L respectively, and the corresponding ranges were 0 – 9.3, 0 – 7.87, 0 – 13.33 and 0 – 62.42 µg/L respectively [17,20,38,154,165,169,173–176,208]. Figure 5.1 shows the component-wise distribution of THMs in Saudi Arabia through boxplots.

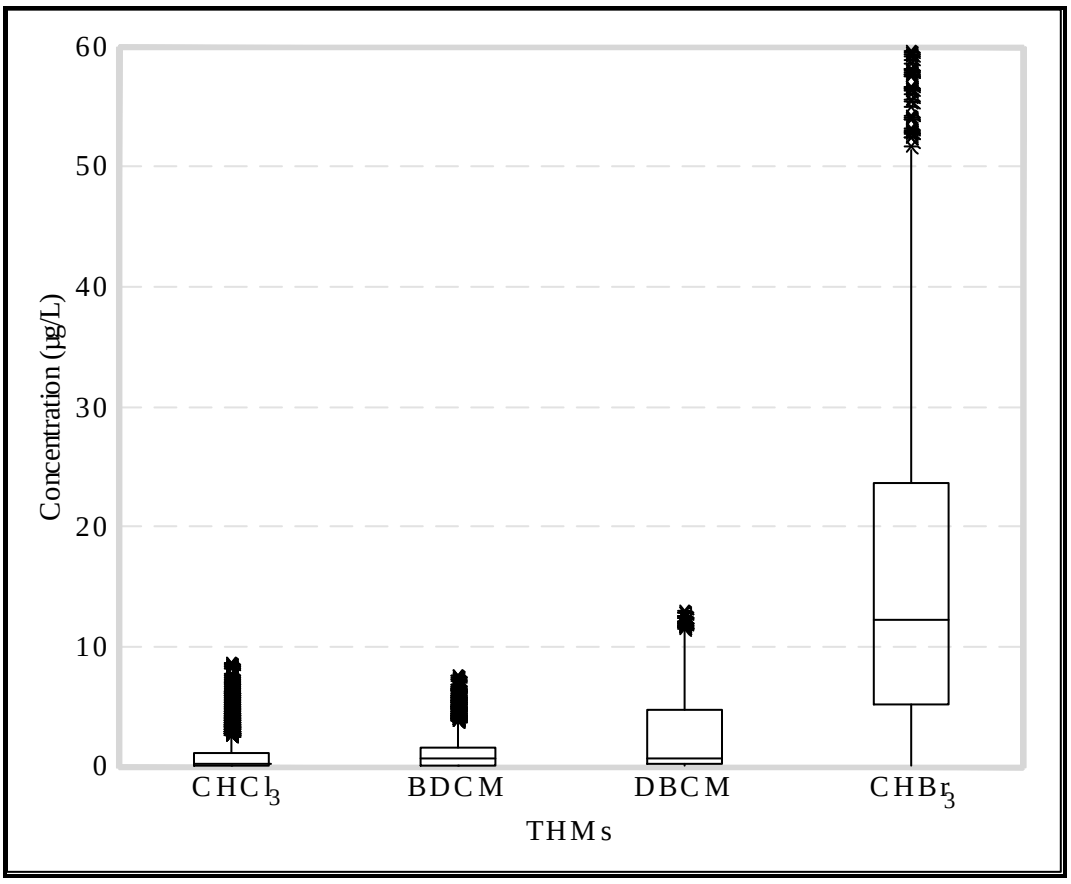


Figure 5.1: Concentration of THMs in desalinated and blended water in Saudi Arabia

The bottom of the box in the figure is the first quartile (Q1): 25% of the data values; the top of the box is the third quartile (Q3): 75% of the data values; the upper whisker extends to the highest data value within the upper limit: Q3 + 1.5*(Q3 – Q1); the lower whisker extends to the lowest value within the lower limit: Q1– 1.5*(Q3 – Q1); Values beyond the whiskers are outliers; the horizontal bar in the middle of box is the median of the data values. On average, $CHCl_3$, BDCM, DBCM, and $CHBr_3$ were approximately 5.2, 6.2, 9.5 and 79.1% respectively. The frequency distribution and the cumulative distribution function of the combined data for different THMs were shown in Figure 5.2–5.5.

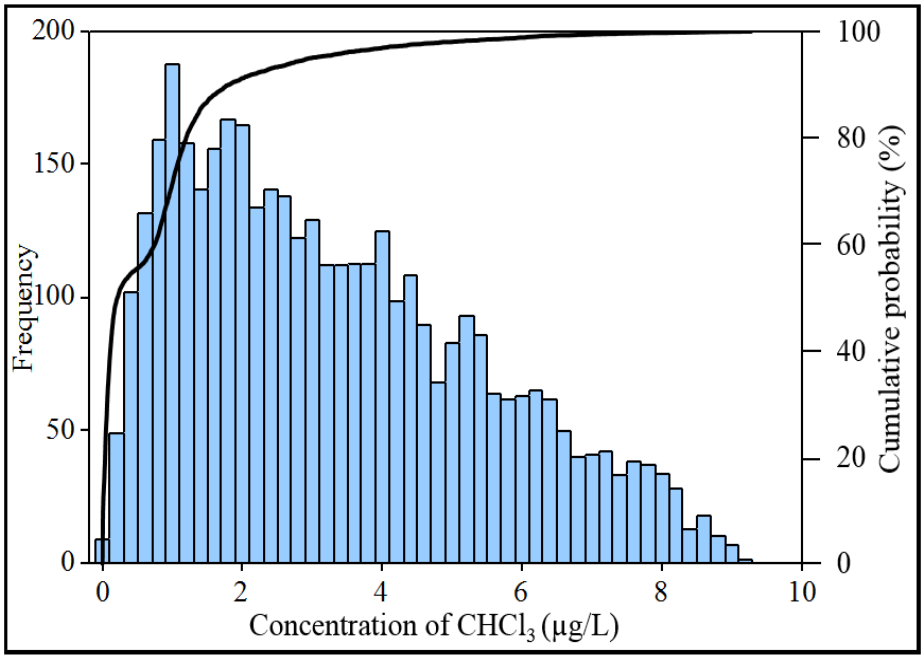


Figure 5.2: Frequency distribution and cumulative distribution function of concentration of $CHCl_3$

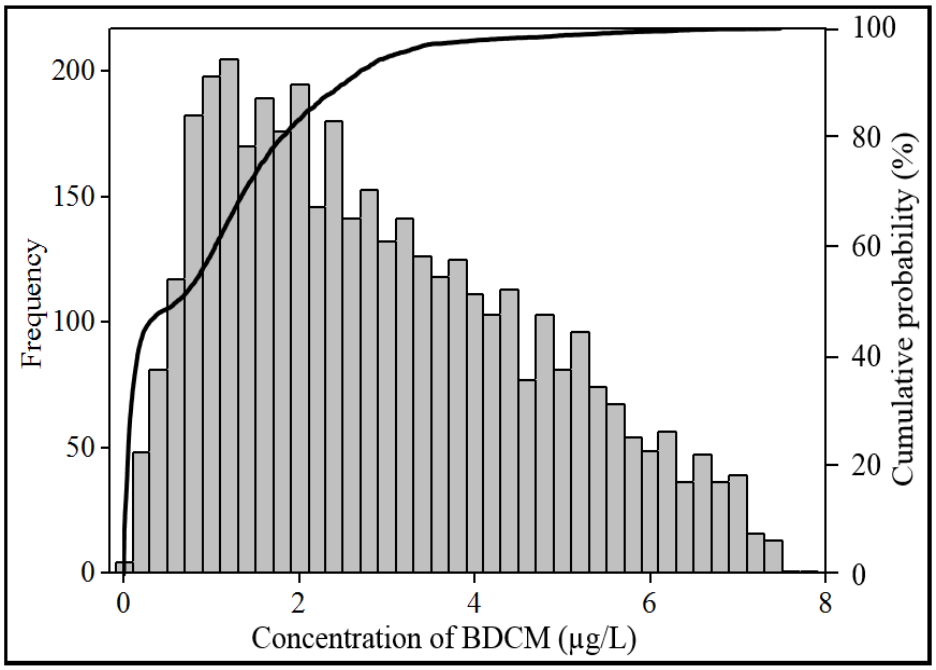


Figure 5.3: Frequency distribution and cumulative distribution function of concentration of BDCM

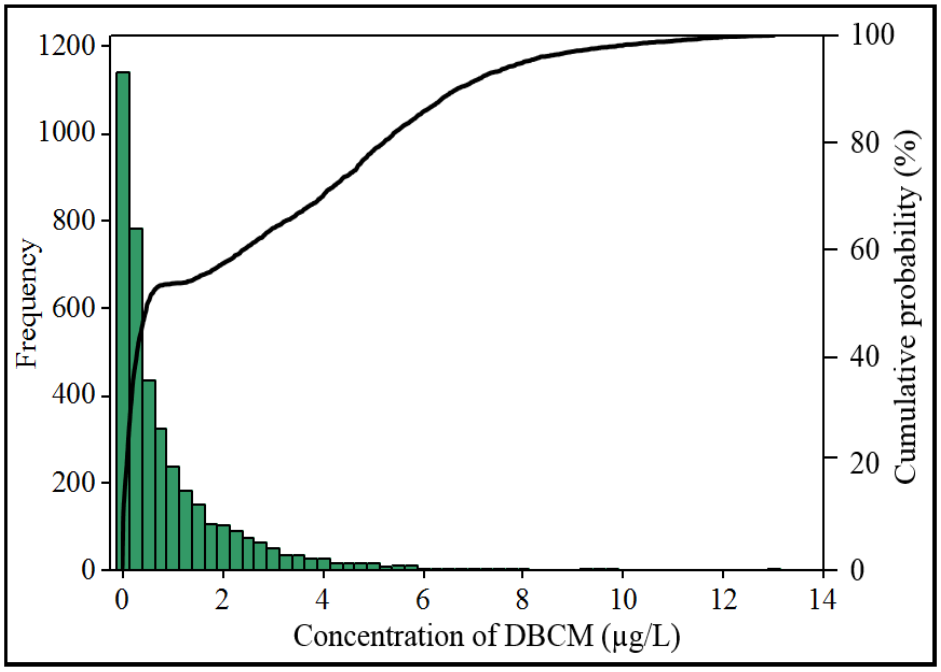


Figure 5.4: Frequency distribution and cumulative distribution function of concentration of DBCM

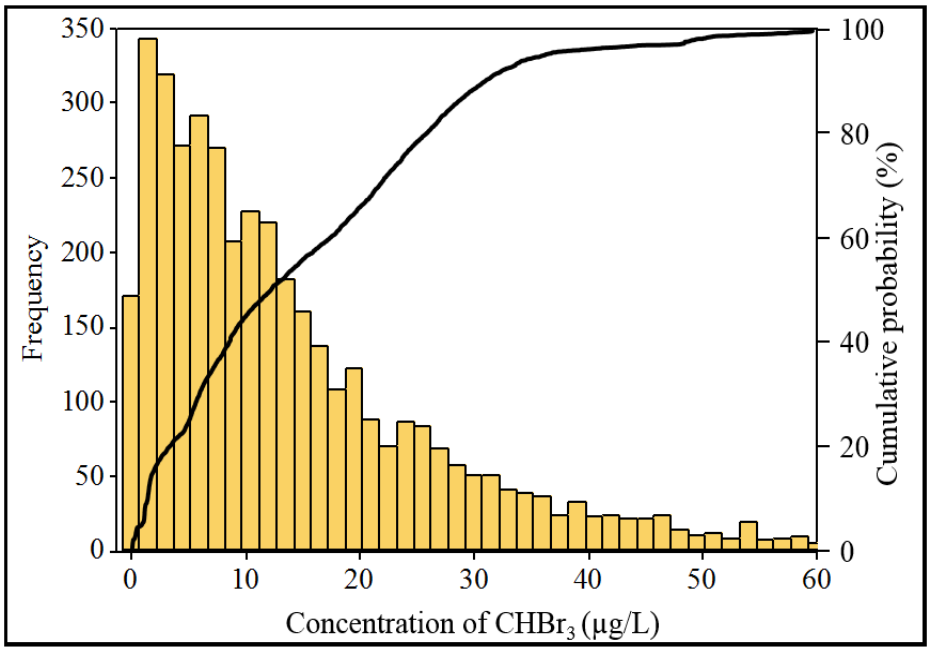


Figure 5.5: Frequency distribution and cumulative distribution function of concentration of $CHBr_3$

Using the combined data, the best-fit statistical distributions were developed for different THM compounds. In this study, concentrations of $CHCl_3$ and BDCM followed triangular distribution while DBCM and $CHBr_3$ followed the Gamma distribution (Table 5.3).

Table 5.3: THMs concentration (µg/L) in desalinated and blended water

THMs	Average	Range	Distribution
$CHCl_3$	0.71	0.0 – 9.30	T(0.0, 0.76, 9.3)
BDCM	0.86	0.0 – 7.87	T(0.0, 0.98, 7.87)
DBCM	1.46	0.0 – 13.33	Gamma(0.4626, 2.028, 0.0111)
$CHBr_3$	15.74	0.0 – 62.42	Gamma(0.043, 13.77)

For the triangular distribution, 1^{st}, 2^{nd}, and 3^{rd} parameters represent the minimum, average and maximum values respectively. In the Gamma distribution, 1^{st}, 2^{nd}, and 3^{rd} parameters represent shape, scale and threshold value, respectively. Following these distributions, 5000 random data were generated using statistical software (e.g., MINITAB^{TM}) to incorporate the data variability. These random data were used in estimating the chronic daily intakes (CDI) of THMs. The other relevant parameters for exposure and risk assessment are shown in Table 5.4 which were discussed in Chapter 4 [35,38]. The exposure scenarios were divided into three age groups (< 2yrs, 2-16 years and 16+ years) following USEPA's methodology [184].

Table 5.4: Values of the different parameters

Parameter	Group	Symbol	Value	References
Water ingestion rate (L/day)	<2 years	IR	0.068, 0.287, 0.735	[191]
	2 - 16 years		0.224, 0.663, 1.649	
	> 16 years		0.74, 1.31, 2.12	
Body weight (kg)	<2 years	BW	9, 11, 14	[191]
	2-16 years		36, 52, 72	
	>16 years		62, 70.4, 81	
Air intake rate (m^3/min)	<2 years	R	0.0026, 0.0034, 0.0043	[191]
	2 -16 years		0.008, 0.011, 0.013	
	>16 years		0.012, 0.014, 0.016	
Area of body skin exposed to water (m^2)	<2 years	S_{skin}	0.46, 0.53, 0.59	[191,211]
	2-16 years		1.25, 1.57, 1.94	
	>16 years		1.69, 1.82, 1.94	
Permeability through skin (m/min)	$CHCl_3$	P_d	$(2.54, 2.67, 2.79) \times 10^{-5}$	[212]
	BDCM		$(2.87, 3.0, 3.13) \times 10^{-5}$	
	DBCM		$(3.25, 3.33, 3.42) \times 10^{-5}$	
	$CHBr_3$		$(3.42, 3.50, 3.58) \times 10^{-5}$	
Molecular weight	$CHCl_3$	MW	119.4	[69]
	BDCM		163.8	
	DBCM		208.3	
	$CHBr_3$		252.8	
Octanol-water partition coefficient	$CHCl_3$	k_{ow}	93	[69]
	BDCM		126	
	DBCM		127	
	$CHBr_3$		128	
THMs concentrations in cold water (µg/L)		C_w	Table 4.3	
Exposure frequency (days/year)		EF	330, 350, 360	[39,191]
Exposure duration (year)		ED	65, 77.1, 82.7	

Parameter	Group	Symbol	Value	References
Averaging time (day)		AT	23725, 28142, 30186	[39,191]
Water flow (L/min)		Q_w	8.7, 10.0, 11.4	[193]
Shower stall volume (m^3)		V	1.67, 2, 2.25	
Shower time (min/shower event)		t	5, 10, 20	
Heated water temperature (°C)		T_2	35, 40, 45	[38,39]
Cold water temperature (°C)		T_1	15, 20, 25	
Air change rate (min^{-1})		k_a	0.018, 0.021, 0.023	[191]
Shower frequency (event/day)		F	0.72, 0.74, 0.76	[191]
Water to air phase transformation rate of THMs (%)		p_v	7.66, 8.76, 9.86	[213]
Absorption efficiency of THMs through respiratory apparatus		E_r	0.7, 0.77, 0.84	[193]
Thickness of stratum corneum (cm)		d_{skin}	0.0015, 0.002, 0.003	[182]

Another important parameter for the assessment of DALY is the proportion and disability weight. In this study, bladder cancer was assumed to be the possible outcome from exposure to THMs. The proportion of various sequelaes and disability weight of the sequelaes were obtained from various studies [194,200,201,206,207,214,215]. The disability weight for various stages of bladder cancer is taken from the various burden of disease studies [194,200,201,214,215]. The sequelaes and disability weights are shown in Table 5.5.

Table 5.5: Proportion and disability weight (DW) for bladder cancer

Sequelae	Proportion (%)	Disability weight (DW)	Reference
Incontinence	5	0.157	[194,200,201,206,207,214,215]
Impotence	10	0.195	[194,200,201,206,207,214,215]
Primary infertility	16	0.18	[194,200,201,214,215]
Secondary infertility	16	0.1	[194,200,201,214,215]

5.2 Results

5.2.1 Chronic Daily Intake

The CDI of THMs through multiple routes of exposure is presented in Table 5.6. The average CDI for THMs were in the order of $CHBr_3$> $CHCl_3$> DBCM > BDCM (Table 5.6). Overall, CDI for $CHCl_3$, DBCM, BDCM, and $CHBr_3$ contributed 13.6, 12.3, 4.1 and 70.0% of total CDI respectively. On average, ingestion, inhalation, and dermal routes contributed approximately 63.4, 22.3, and 14.3% of total CDI respectively and their ranges were 65.2 – 86.2, 10.0 – 34.6, and 3.8 – 20.5% respectively (Table 5.6).

Table 5.6: CDI of THMs for different routes (mg/kg-day)

THMs	Pathways	Average	Minimum	Maximum	Std. Dev.
$CHCl_3$	Ingestion	5.64×10^{-5}	3.93×10^{-7}	2.12×10^{-4}	3.78×10^{-5}
	Inhalation	2.00×10^{-5}	2.20×10^{-7}	1.29×10^{-4}	1.78×10^{-5}
	Dermal	7.41×10^{-6}	9.33×10^{-9}	5.56×10^{-5}	8.25×10^{-6}
	Total	8.38×10^{-5}	6.22×10^{-7}	3.97×10^{-4}	5.79×10^{-5}
BDCM	Ingestion	5.16×10^{-5}	8.73×10^{-7}	1.79×10^{-4}	3.30×10^{-5}
	Inhalation	1.83×10^{-5}	2.61×10^{-7}	1.26×10^{-4}	1.58×10^{-5}
	Dermal	5.77×10^{-6}	5.73×10^{-9}	5.18×10^{-5}	7.41×10^{-6}
	Total	7.57×10^{-5}	1.14×10^{-6}	3.57×10^{-4}	4.99×10^{-5}
DBCM	Ingestion	1.75×10^{-5}	1.05×10^{-7}	2.70×10^{-4}	2.61×10^{-5}
	Inhalation	6.21×10^{-6}	1.48×10^{-8}	1.96×10^{-4}	1.09×10^{-5}
	Dermal	1.67×10^{-6}	4.35×10^{-10}	6.80×10^{-5}	4.17×10^{-6}
	Total	2.54×10^{-5}	1.20×10^{-7}	5.33×10^{-4}	3.86×10^{-5}
$CHBr_3$	Ingestion	2.65×10^{-4}	4.51×10^{-7}	2.68×10^{-3}	2.70×10^{-4}
	Inhalation	9.33×10^{-5}	1.49×10^{-8}	1.34×10^{-3}	1.12×10^{-4}
	Dermal	7.31×10^{-5}	1.62×10^{-8}	8.98×10^{-4}	7.65×10^{-5}
	Total	4.32×10^{-4}	7.62×10^{-8}	4.92×10^{-3}	4.36×10^{-4}

The lifetime average CDI of $CHCl_3$, BDCM, DBCM and $CHBr_3$ through all routes were 8.38×10^{-5}, 7.57×10^{-5}, 2.54×10^{-5}, and 4.32×10^{-4} mg/kg-day respectively while their ranges were 6.22×10^{-7} – 3.97×10^{-4}, 1.14×10^{-6} – 3.57×10^{-4}, 1.20×10^{-7} – 5.33×10^{-4}, and 7.62×10^{-8} – 4.92×10^{-3} mg/kg-day respectively. The CDI of $CHCl_3$ through ingestion, inhalation and dermal pathways were 5.64×10^{-5} (range: 3.93×10^{-7} – 2.12×10^{-4}), 2.00×10^{-5} (range: 2.20×10^{-7} – 1.29×10^{-4}), and 7.41×10^{-6} (range: 9.33×10^{-9} – 5.56×10^{-5}) respectively. The CDI of BDCM through ingestion, inhalation and dermal pathways were 5.16×10^{-5} (range: 8.73×10^{-7} – 1.79×10^{-4}), 1.83×10^{-5} (range: 2.61×10^{-7} – 1.26×10^{-4}), and 5.77×10^{-6} (range:

5.73×10^{-9} – 5.18×10^{-5}) respectively. The CDI of DBCM through ingestion, inhalation and dermal pathways were 1.75×10^{-5} (range: 1.05×10^{-7} – 2.70×10^{-4}), 6.21×10^{-6} (range: 1.48×10^{-8} – 1.96×10^{-4}), and 1.67×10^{-6} (range: 4.35×10^{-10} – 6.80×10^{-5}) respectively. The CDI of $CHBr_3$ through ingestion, inhalation and dermal pathways were 2.65×10^{-4} (range: 4.51×10^{-7} – 2.68×10^{-3}), 9.33×10^{-5} (range: 1.49×10^{-8} – 1.34×10^{-3}), and 7.31×10^{-5} (range: 1.62×10^{-8} – 8.98×10^{-4}) respectively. The frequency distribution of CDI for THMs through all routes are shown in Figures 5.6– 5.9. The CDI of $CHCl_3$ followed a lognormal distribution with location and scale of -10.20 and 0.70 mg/kg-day respectively (Figure 5.6). The CDI of DBCM also followed a lognormal distribution with location and scale of -11.69 and 1.72 mg/kg-day respectively (Figure 5.7). The CDI of BDCM and $CHBr_3$ followed Gamma distribution. The shape and scale for BDCM were 2.15 and 3.5×10^{-5} mg/kg-day and for $CHBr_3$, these parameters were 1.03 and 4.2×10^{-4} mg/kg-day respectively (Figure 5.8 and Figure 5.9). The frequency distributions for $CHCl_3$, BDCM, DBCM and $CHBr_3$ showed skewed distributions with right sided long tail, indicating that these fractions of data might pose elevated risk to humans.

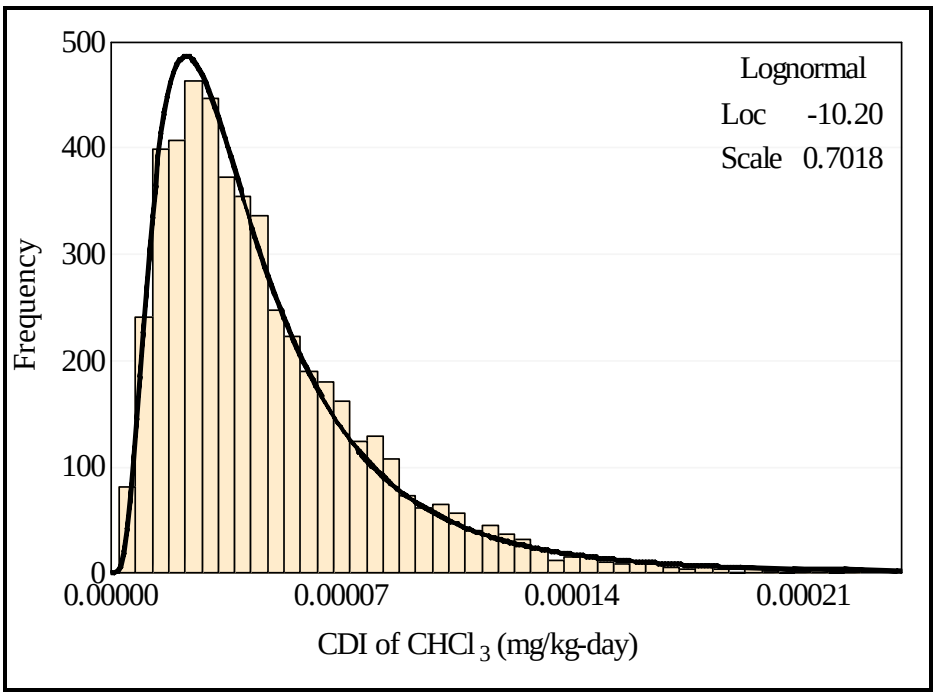


Figure 5.6: Frequency distribution and fit of CDI of $CHCl_3$

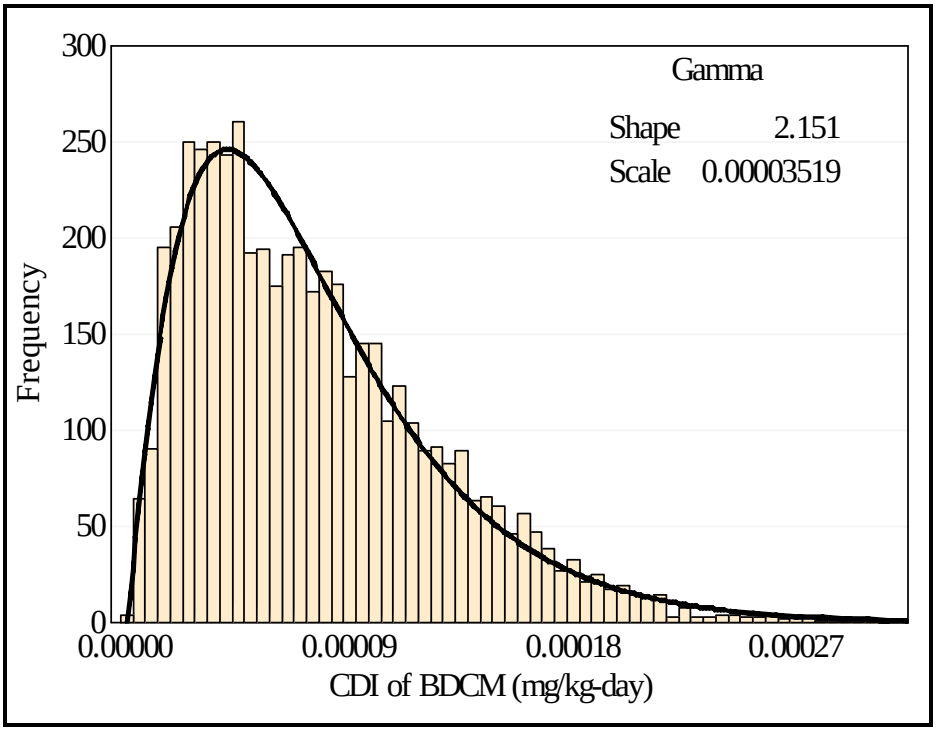


Figure 5.7: Frequency distribution and fit of CDI of BDCM

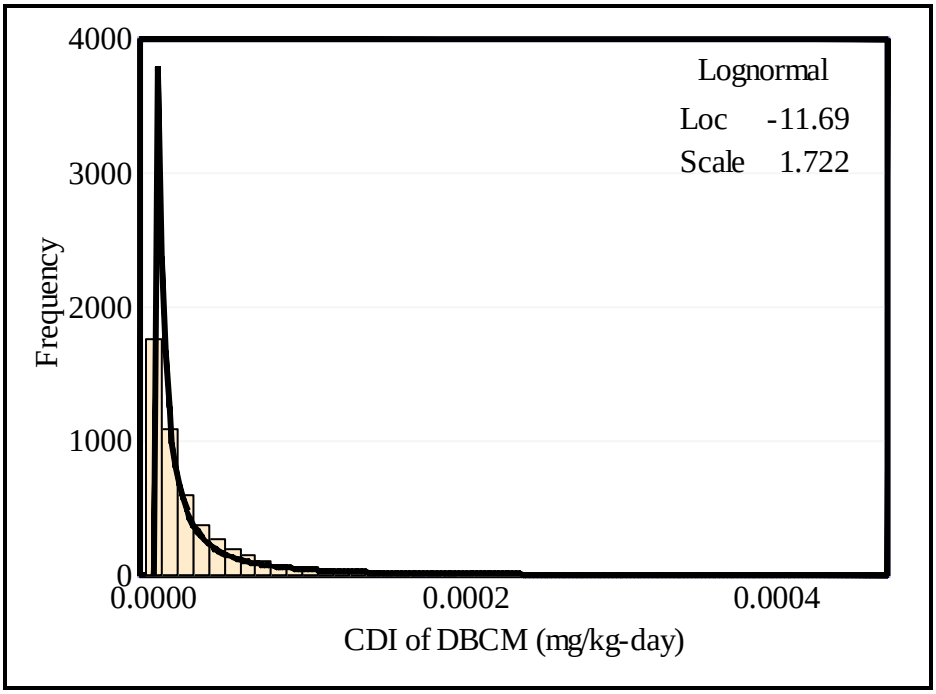


Figure 5.8: Frequency distribution and fit of CDI of DBCM

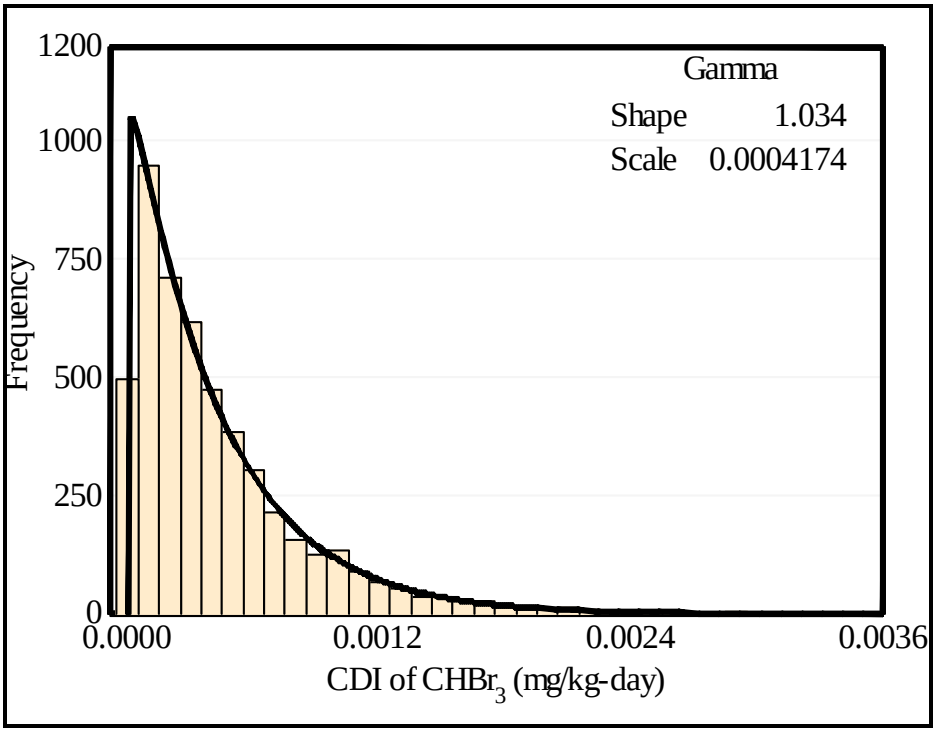


Figure 5.9: Frequency distribution and fit of CDI of $CHBr_3$

The average CDI for all THMs ($CHCl_3$, BDCM, DBCM and $CHBr_3$) for the age group <2 years, 2 – 16 years, and >16 years were 2.73×10^{-5}, 1.06×10^{-4}, and 4.84×10^{-4} mg/kg-day respectively while their ranges were 6.32×10^{-7} – 2.25×10^{-4}, 2.78×10^{-6} – 1.03×10^{-3}, and 1.64×10^{-5} – 3.21×10^{-3} mg/kg-day respectively (Figure 5.10). The standard deviation of CDI of <2 years, 2 – 16 years and >16 years were 2.16×10^{-5}, 8.29×10^{-5}, and 3.58×10^{-4}mg/kg-day respectively. The largest contributor to the CDI was the age group >16 years (78.43%), followed by 2 – 16 years (17.15%) and <2 years (4.42%). Combining all age groups the average CDI was 6.17×10^{-4} mg/kg-day with the ranges of 1.98×10^{-5} – 4.40×10^{-3}mg/kg-day and standard deviation of 4.52×10^{-4} mg/kg-day (Figure 5.10).

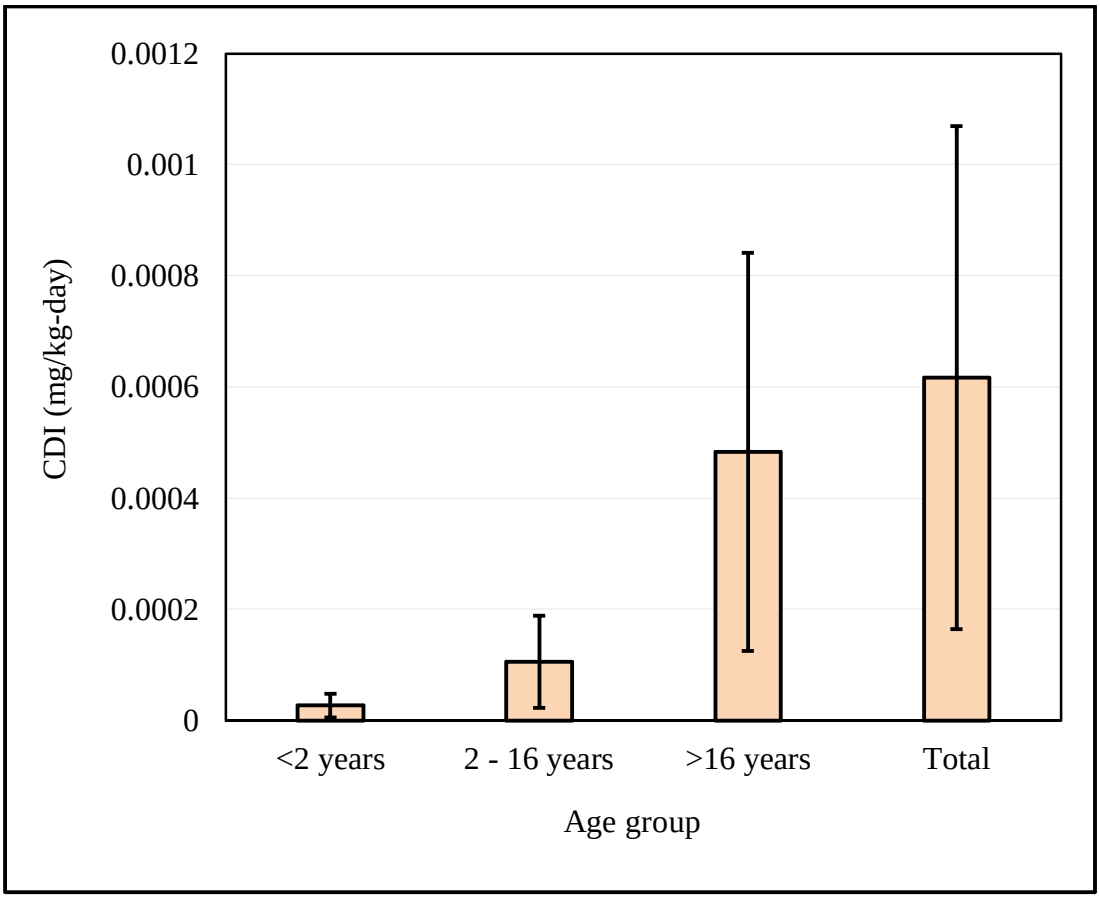


Figure 5.10: Average CDI of all THMs for different age group. Error bars represent standard deviation

The CDI for different THMs for different age groups is summarized in Table 5.7. The CDI of $CHCl_3$ for age group <2 years, 2 – 16 years, and >16 years were 3.71×10^{-6} (range: 2.94×10^{-8} – 1.80×10^{-5}), 1.42×10^{-5} (range: 1.37×10^{-7} – 6.93×10^{-5}), and 6.60×10^{-5} (range: 6.37×10^{-7} – 2.97×10^{-4}) respectively (Table 5.7). The CDI of BDCM for age group <2 years, 2 – 16 years, and >16 years were 3.32×10^{-6} (range: 5.81×10^{-8} – 1.69×10^{-5}), 1.28×10^{-5} (range: 2.17×10^{-7} – 6.10×10^{-5}), and 5.96×10^{-5} (range: 8.13×10^{-7} – 2.64×10^{-4}) respectively (Table 5.7). The CDI of DBCM for age group <2 years, 2 – 16 years, and >16 years were 1.11×10^{-6} (range: 3.89×10^{-9} – 2.49×10^{-5}), 4.22×10^{-6} (range: 1.71×10^{-8} – 8.18×10^{-5}), and 2.00×10^{-5} (range: 1.07×10^{-7} – 3.77×10^{-4}) respectively (Table 5.7). The CDI of $CHBr_3$ for age group <2 years, 2 – 16 years, and >16 years were 1.91×10^{-5} (range: 2.79×10^{-9} – 2.13×10^{-4}), 7.46×10^{-5} (range: 1.33×10^{-8} – 9.21×10^{-4}), and 3.38×10^{-4} (range: 6.72×10^{-8} – 3.02×10^{-3}) respectively (Table 5.7).

Table 5.7: CDI of THMs for different age groups (mg/kg-day)

THMs	Age group	Average	Minimum	Maximum	Std. Dev.
$CHCl_3$	<2 years	3.71×10^{-6}	2.94×10^{-8}	1.80×10^{-5}	2.77×10^{-6}
	2-16 years	1.42×10^{-5}	1.37×10^{-7}	6.93×10^{-5}	1.06×10^{-5}
	>16 years	6.60×10^{-5}	6.37×10^{-7}	2.97×10^{-4}	4.60×10^{-5}
BDCM	<2 years	3.32×10^{-6}	5.81×10^{-8}	1.69×10^{-5}	2.38×10^{-6}
	2-16 years	1.28×10^{-5}	2.17×10^{-7}	6.10×10^{-5}	9.22×10^{-6}
	>16 years	5.96×10^{-5}	8.13×10^{-7}	2.64×10^{-4}	3.97×10^{-5}
DBCM	<2 years	1.11×10^{-6}	3.89×10^{-9}	2.49×10^{-5}	1.76×10^{-6}
	2-16 years	4.22×10^{-6}	1.71×10^{-8}	8.18×10^{-5}	6.57×10^{-6}
	>16 years	2.00×10^{-5}	1.07×10^{-7}	3.77×10^{-4}	3.07×10^{-5}
$CHBr_3$	<2 years	1.91×10^{-5}	2.79×10^{-9}	2.13×10^{-4}	2.04×10^{-5}
	2-16 years	7.46×10^{-5}	1.33×10^{-8}	9.21×10^{-4}	7.86×10^{-5}
	>16 years	3.38×10^{-4}	6.72×10^{-8}	3.02×10^{-3}	3.43×10^{-4}

The frequency distribution of CDI for all THMs of all age groups are shown in Figure 5.11– 5.13.

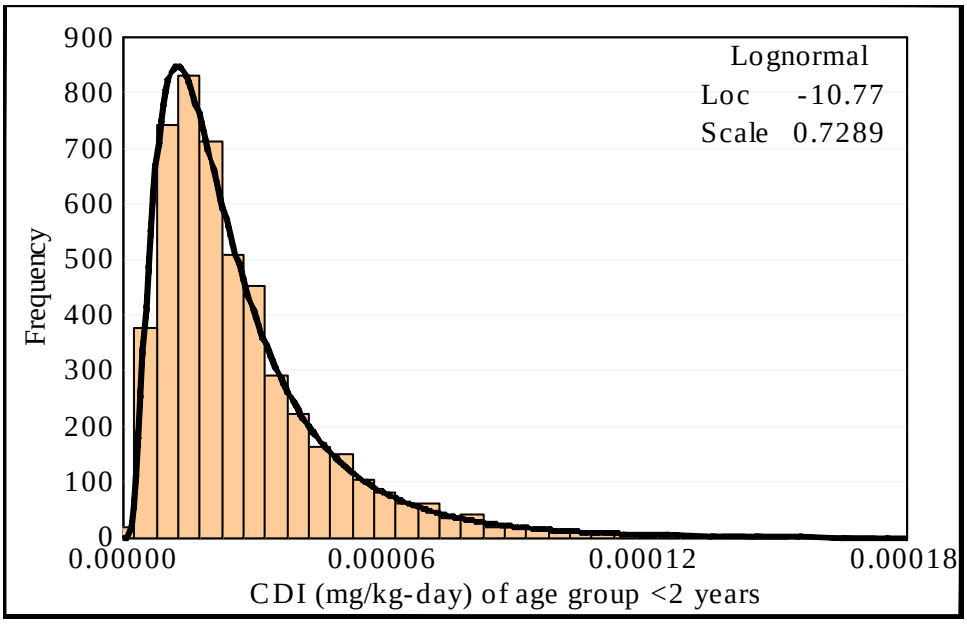


Figure 5.11: Frequency distribution and fit of CDI combining all THMs of age group <2 years

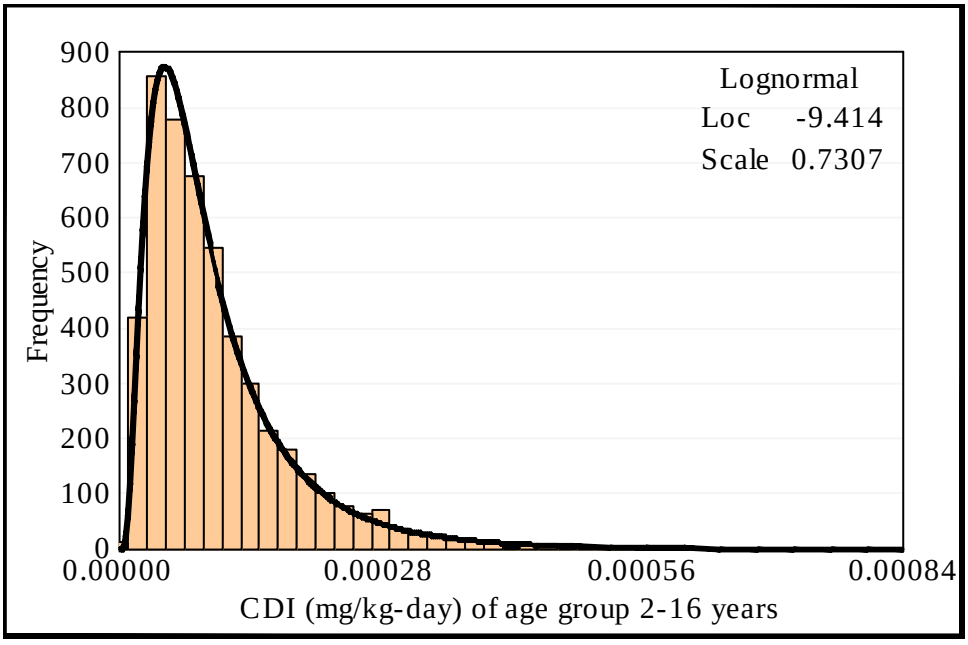


Figure 5.12: Frequency distribution and fit of CDI combining all THMs of age group 2-16 years

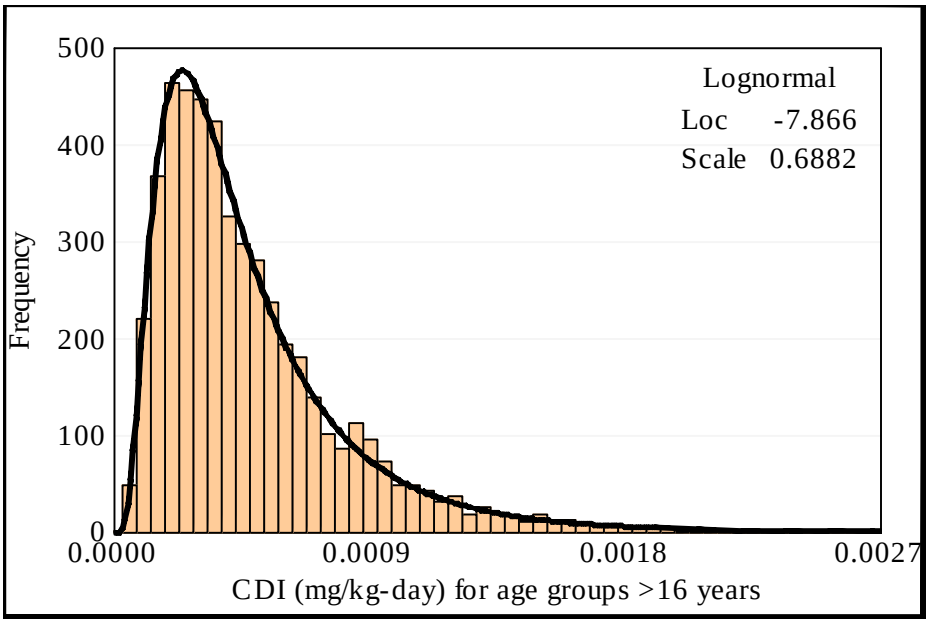


Figure 5.13: Frequency distribution and fit of CDI combining all THMs of age group >16 years

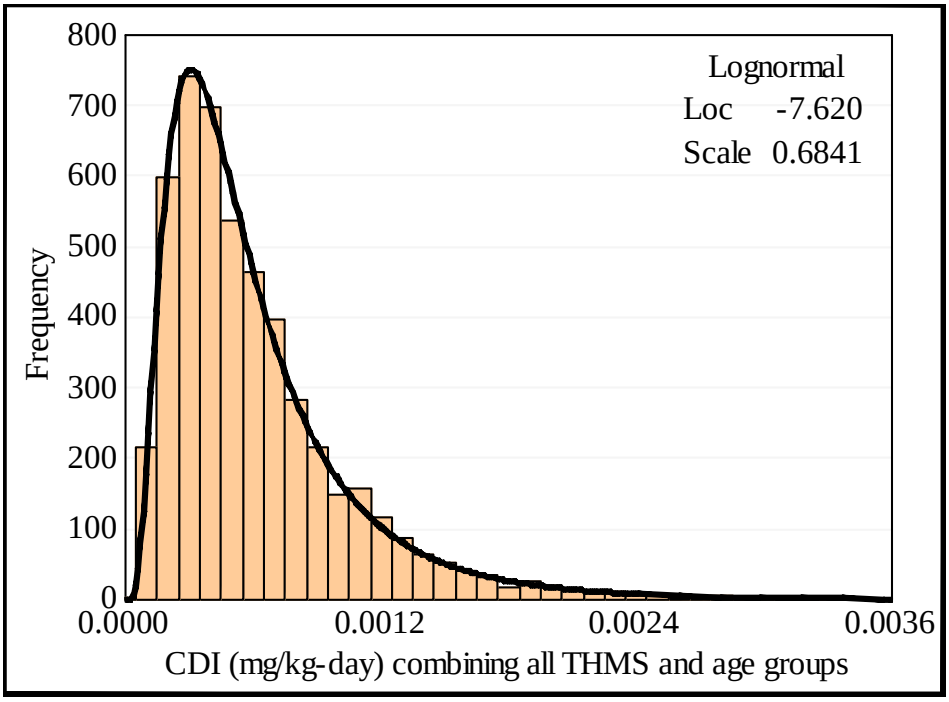


Figure 5.14: Frequency distribution and fit of CDI combining all THMs and age groups

The CDI of age group <2 years followed a lognormal distribution with location and scale of -10.77 and 0.73 mg/kg-day respectively (Figure 5.11). The CDI of age group 2– 16 years also followed a lognormal distribution with location and scale of -9.41 and 0.73 mg/kg-day respectively (Figure 5.12). The CDI of age group >16 years followed a lognormal distribution. The location and scale for CDI of THMs were -7.87 and 0.69 mg/kg-day respectively (Figure 5.13). Combining all age groups the CDI followed a lognormal distribution with location and scale of -7.62 and 0.68 mg/kg-day respectively (Figure 5.14). The frequency distributions for all age groups showed skewed distributions with right sided long tail, indicating that these fractions of data might pose elevated risk to human.

5.2.2 Risks of THMs

Cancer and non-cancer risks were estimated for the ingestion, inhalation, and dermal contact pathways. In estimating lifetime excess cancer risk from THMs, $CHCl_3$ was excluded following USEPA's exclusion of $CHCl_3$ from the list of possible or probable human carcinogens through oral route [139]. However, hazard indices were predicted for the four THMs ($CHCl_3$, BDCM, DBCM and $CHBr_3$) as recommended by the USEPA [139]. The lifetime excess cancer risks and hazard indices are shown in Table 5.8. The average cancer risk considering all age groups was predicted to be 1.78×10^{-5} with a range of $7.40\times10^{-7} – 9.26\times10^{-5}$. The cancer risks for ingestion, inhalation, and dermal routes were 1.16×10^{-5} (range: $5.76\times10^{-7} – 5.26\times10^{-5}$), 4.17×10^{-6} (range: $1.11\times10^{-7} – 3.54\times10^{-5}$), and 1.97×10^{-6} (range: $1.31\times 10^{-8} – 1.35\times10^{-5}$) respectively (Table 5.8). The ingestion, inhalation, and dermal routes contributed approximately 65.4%, 23.5%, and 11.1% of overall cancer risks. The overall hazard index was estimated to be 3.49×10^{-2} with the range of $1.20\times10^{-3} – 2.34\times10^{-1}$. Hazard indices through ingestion, inhalation, and dermal routes

were estimated to be 2.23×10^{-2} (range: 1.05×10^{-3} – 1.45×10^{-1}), 7.89×10^{-3} (range: 1.21×10^{-4} – 8.18×10^{-2}), and 4.77×10^{-3} (range: 3.84×10^{-5} – 4.53×10^{-2}) respectively (Table 5.8). Among the 5000 simulated scenarios, hazard indices were always lower than the critical value of unity.

Table 5.8: Cancer risks and hazard indices for exposure to THMs

Pathways	Cancer Risk				Hazard Index			
	Average	Std. Dev.	Minimum	Maximum	Average	Std. Dev.	Minimum	Maximum
Ingestion	1.16×10^{-5}	6.53×10^{-6}	5.76×10^{-7}	5.26×10^{-5}	2.23×10^{-2}	1.45×10^{-2}	1.05×10^{-3}	1.45×10^{-1}
Inhalation	4.17×10^{-6}	3.31×10^{-6}	1.11×10^{-7}	3.54×10^{-5}	7.89×10^{-3}	6.70×10^{-3}	1.21×10^{-4}	8.18×10^{-2}
Dermal	1.97×10^{-6}	1.59×10^{-6}	1.31×10^{-8}	1.35×10^{-5}	4.77×10^{-3}	3.90×10^{-3}	3.84×10^{-5}	4.53×10^{-2}
Total	1.78×10^{-5}	1.02×10^{-5}	7.40×10^{-7}	9.26×10^{-5}	3.49×10^{-2}	2.33×10^{-2}	1.20×10^{-3}	2.34×10^{-1}

With respect to age groups, average cancer risks during <2 years, 2 – 16 years, and >16 years were 4.5×10^{-6}, 5.2×10^{-6}, and 8.0×10^{-6} respectively with the ranges of 9.52×10^{-8} – 2.87×10^{-5}, 1.68×10^{-7} – 3.01×10^{-5}, and 3.55×10^{-7} – 4.35×10^{-5} respectively (Figure 5.15). The standard deviations of cancer risk of these three age groups were 2.86×10^{-6}, 3.31×10^{-6}, and 4.75×10^{-6} respectively (Figure 5.15). These three age groups contributed approximately 25.4%, 29.3%, and 45.3% of total cancer risks respectively (Figure 5.15). In the early life, despite the exposure was only for 2 years, it contributed 25.4% of the overall risk, indicating that appropriate protection during this period (birth to < 2 years) might reduce the overall risk significantly.

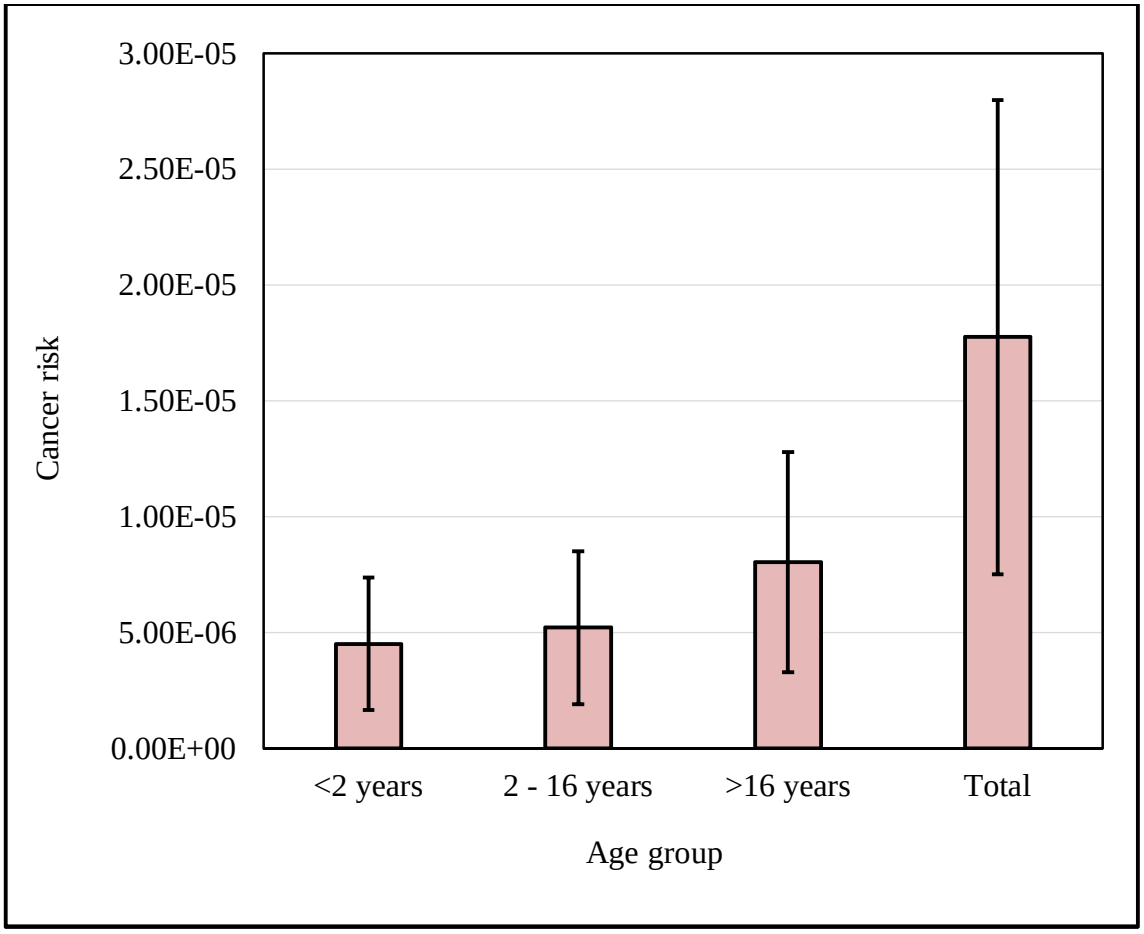


Figure 5.15: Average cancer risk for different age groups. Error bars represent standard deviation

For the hazard indices, average hazard index during <2 years, 2 – 16 years, and >16 years were 1.55×10^{-3}, 5.99×10^{-3}, and 2.75×10^{-2} respectively with the ranges of 3.83×10^{-5} – 1.17×10^{-2}, 1.69×10^{-4} – 5.49×10^{-2}, and 9.99×10^{-4} – 1.72×10^{-1} respectively (Figure 5.16). The standard deviation of hazard index of these three age groups were 1.12×10^{-3}, 4.31×10^{-3}, and 1.85×10^{-2} respectively (Figure 5.16). These three age groups contributed approximately 4.42%, 17.12%, and 78.46% of total hazard indices respectively (Figure 5.16).

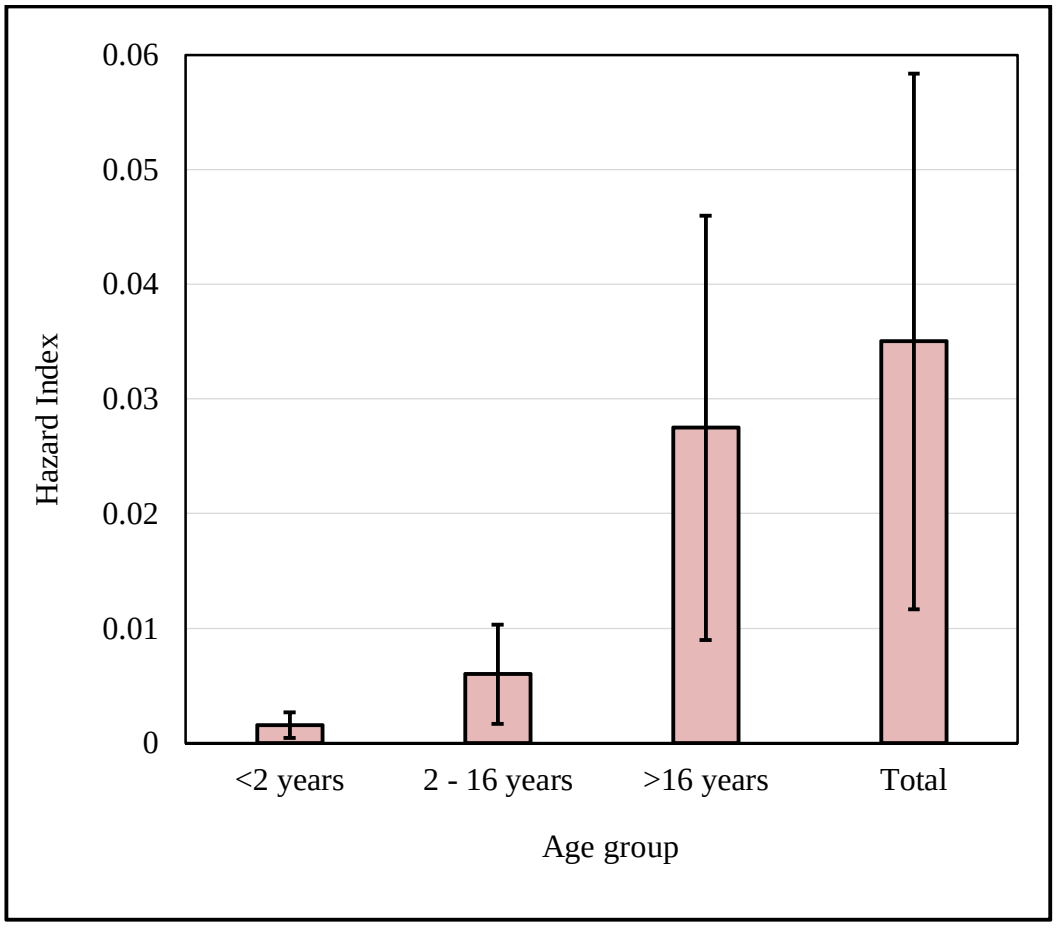


Figure 5.16: Average hazard index for different age groups. Error bars represent standard deviation

The frequency distribution of the overall cancer risk follows a lognormal distribution with the location of -11.10 and scale of 0.60 (Figure 5.17). The cumulative distribution function of cancer risk showed that the probability of having cancer risk equal to or less than 4×10^{-5}, 5×10^{-5}, and 6×10^{-5} were 96.5%, 99%, and 100% respectively, which is denoted by point a, b, c in the Figure 5.17.

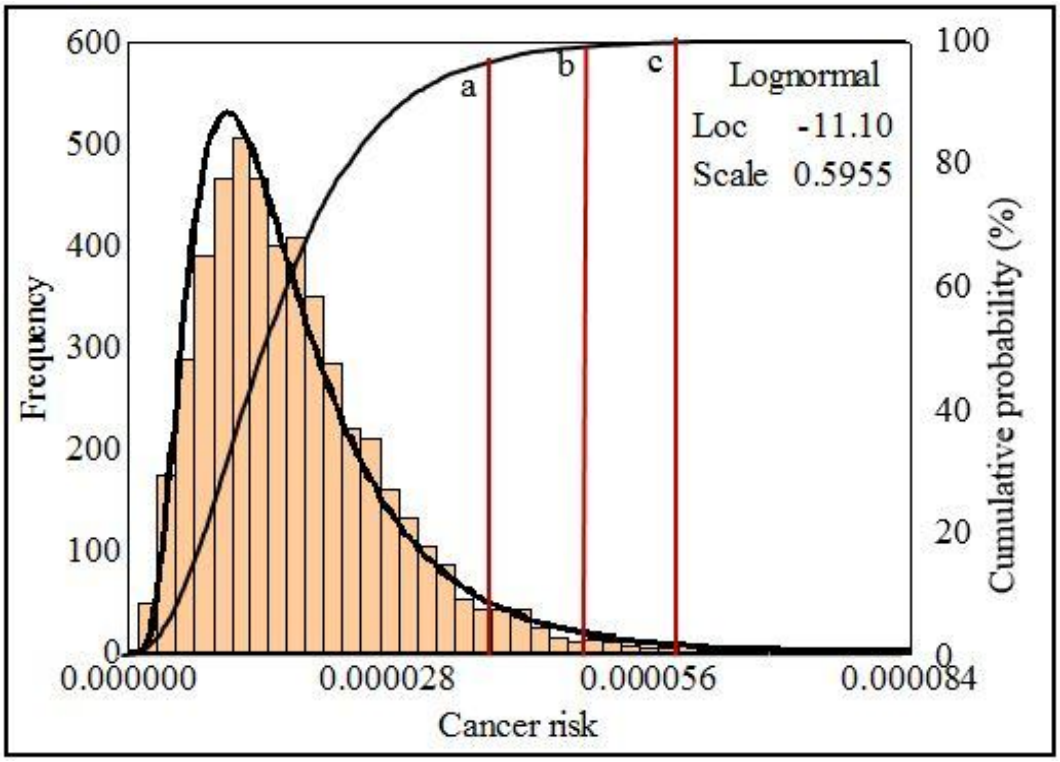


Figure 5.17: Frequency distribution and fit of cancer risk

Cancer risks exceedance probabilities are presented in Figure 5.18. In 100% cases, cancer risks were predicted to exceed the risk level of 1.0×10^{-6} (Figure 5.18), meaning that at least 1.0 cancer incident in a million can be seen from lifetime exposure to THMs. At the risk levels of 5.0×10^{-6}, 1.0×10^{-5}, 5.0×10^{-5} and 1.0×10^{-4}, cancer risks exceedance probabilities were 95.5%, 77.5%, 1.2%, and 0% respectively, indicating that there were 100%, 95.5%, 77.5%, 1.2%, and 0% chances of having 1, 5, 10, 50 and 100 cancer incidents in a million (Figure 5.18). So, there was 100% chance of exceeding the recommended value of 1.0×10^{-6} set by USEPA [216].

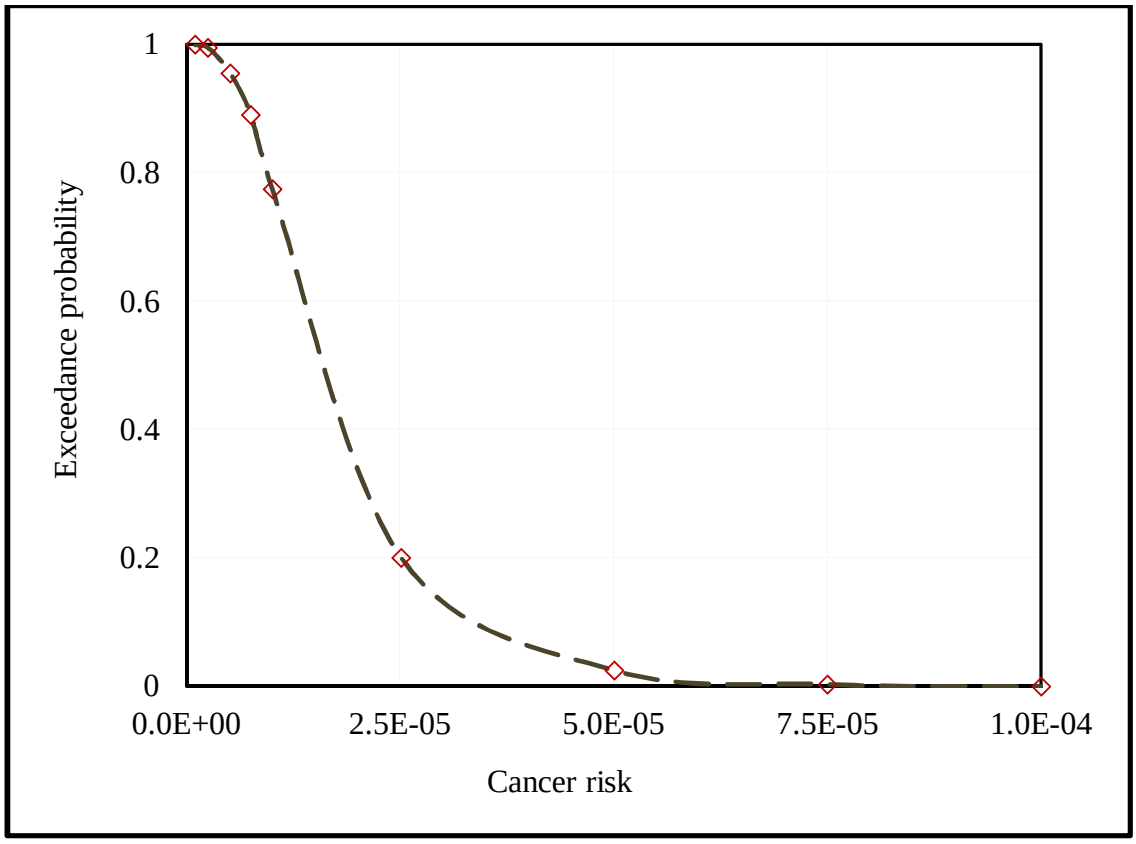


Figure 5.18: Exceedance probability of cancer risk

5.2.3 Disability Adjusted Life Years (DALY)

The overall DALY was estimated to be 25.1 with the range of 23.2 – 26.8, meaning that on average 25.1 years are likely to be lost due to the elevated cancer risks from exposure to THMs (Table 5.9). Among the DALY, the YLL and YLD were estimated to be 18.6 (17.1 – 19.9) and 6.5 (6.0 – 6.9) respectively (Table 5.9). The YLL and YLD contributed approximately 74% and 26% of total DALY (Table 5.9). Based on the age-specific bladder cancer incident rates in Saudi Arabia [203], the YLL and YLD were estimated for the age-groups of 0-14, 15-39, 40-44, 45-49, 50-54, 55-59, 60-64, 65-69, 70-74 and 75+ ages. In Saudi Arabia, total populations in 2014 were estimated to be 31 million [217].

Table 5.9: DALY for exposure to THMs

	Average	Minimum	Maximum	Std. Dev.
YLL (year)	18.56	17.14	19.93	0.44
YLD (year)	6.50	6.03	6.93	0.16
DALY (year)	25.06	23.18	26.84	0.58

The total populations in the specific age groups were obtained from the world factbook of Central Intelligence Agency (CIA) database [1]. The YLL and YLD for different age groups are shown in Figure 5.19. The largest DALY (5.6) were estimated for 15-39 age group. The age groups of 15-39, 40-44, 45-49, 50-54 and 55-59 were the main contributors of DALY (Figure 5.19).

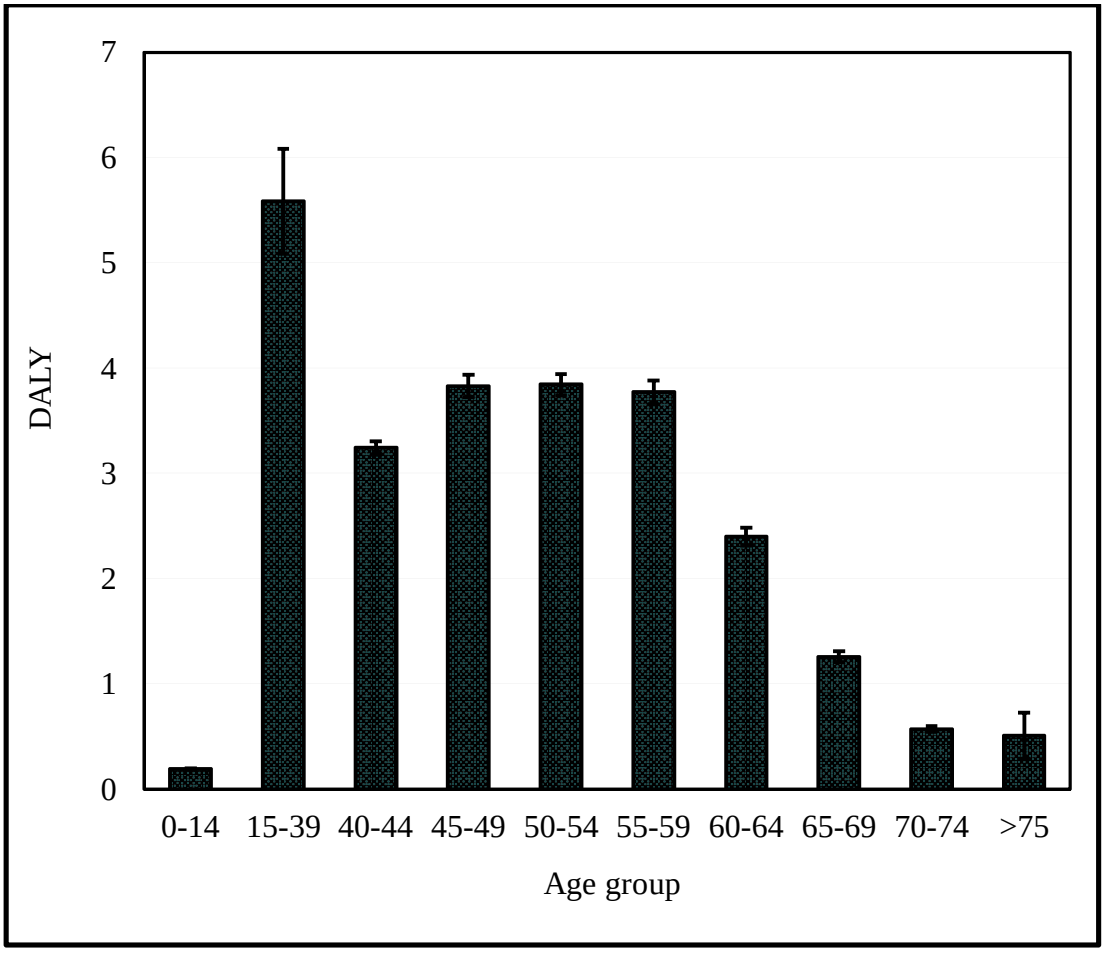


Figure 5.19: DALYs for different age groups. Error bars represent standard deviation

The total DALY (25.1) was divided by the total populations (31 million) to obtain cancer risk per person per year (PPPY) in terms of DALY. The cancer risk in terms of DALY was obtained as 8.48×10^{-7} PPPY, which was lower than the WHO guideline value of 1.0×10^{-6} [218]. This value is often used as the target for health safeguard [219]. The World Health Organization (WHO) has estimated the loss per DALY in terms of monetary value [220–222]. One DALY was associated with a loss of US$108,600 [220–222], which means one year of healthy human life costs US$108,600. Using these data, the total financial burden was estimated for Saudi Arabia to be US$ 2.72 million with the range of US$ 2.52 – 2.91 million.

5.3 Controlling Risks of DBPs

The predicted cancer risks might be sensitive to several parameters. With the view of controlling the risk of DBPs, sensitivity analysis was performed by varying three parameters: shower stall volume (*V*), air exchange rate (*K*), and shower duration (*t*) while the other parameters were kept constant. Cancer risks were found to be sensitive to *V*, *K* and *t*. Shower duration (*t*) affects both inhalation and dermal risks. Inhalation risk was increased with increase in shower duration (*t*) following the polynomial law. The inhalation risk can be represented as:

$$\mathrm{Risk}_{\mathrm{Inh}} = 7 \times 10^{-9}\, t^2 + 5 \times 10^{-8}\, t + 3 \times 10^{-7} \qquad (5.1)$$

Where, *t* = shower duration (min)

The dermal risk also increases with the increase in shower duration following the polynomial law, which can be expressed as:

$$\text{Risk}_{\text{Der}} = 7 \times 10^{-9} t^2 + 6 \times 10^{-8}\, t + 2 \times 10^{-7} \quad (5.2)$$

Combining the two pathways (inhalation + dermal), an increase in cancer risk with shower duration was found to follow the polynomial law (Figure 5.20) as:

$$\text{Risk}_{\text{Inh+Der}} = 10^{-8} t^2 + 10^{-7} t + 5 \times 10^{-7} \quad (4.3)$$

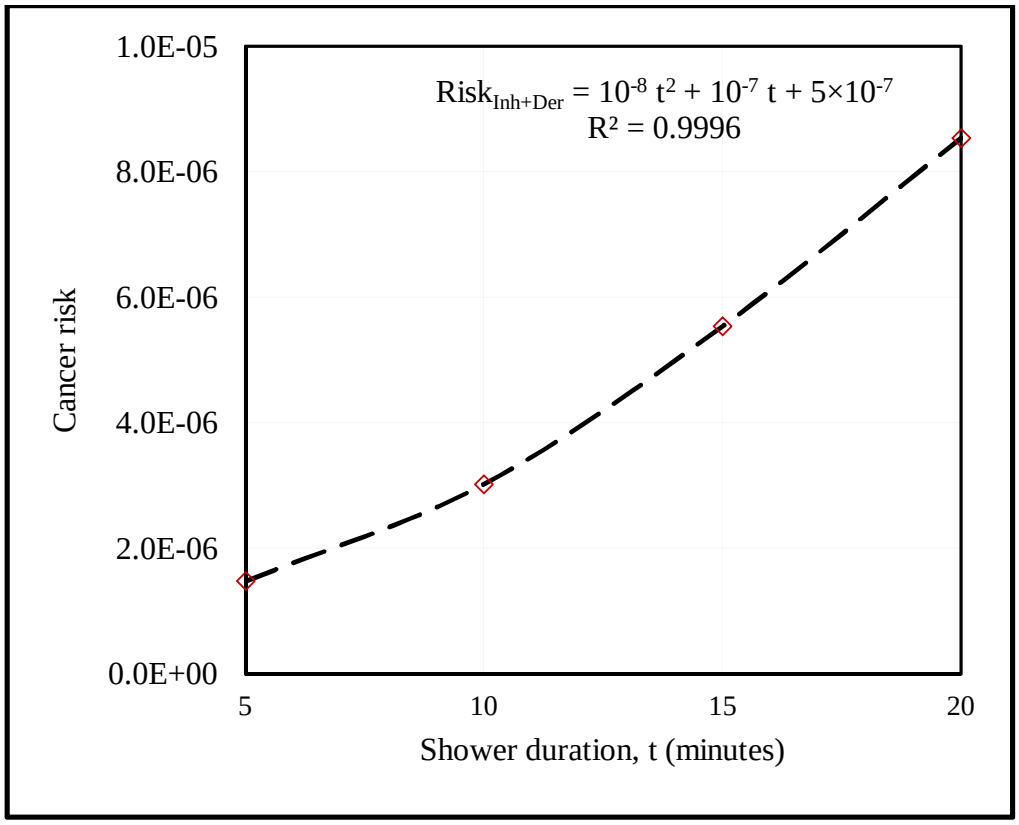


Figure 5.20: Combined effects of shower duration on inhalation and dermal cancer risk

Shower stall volume (V) and air exchange rate (K) have effects on inhalation risk. The increase in V and K decreased inhalation risk following the power law equations (Figure 5.21 and Figure 5.22), which can be presented as:

$$\text{Risk}_{\text{Inh}} = 8 \times 10^{-6} V^{-1.001} \quad (5.4)$$

$$\text{Risk}_{\text{Inh}} = 3 \times 10^{-6} k_a{}^{-0.124} \quad (5.5)$$

Where, V = shower stall volume (m^3), k_a = air exchange rate (min^{-1}).

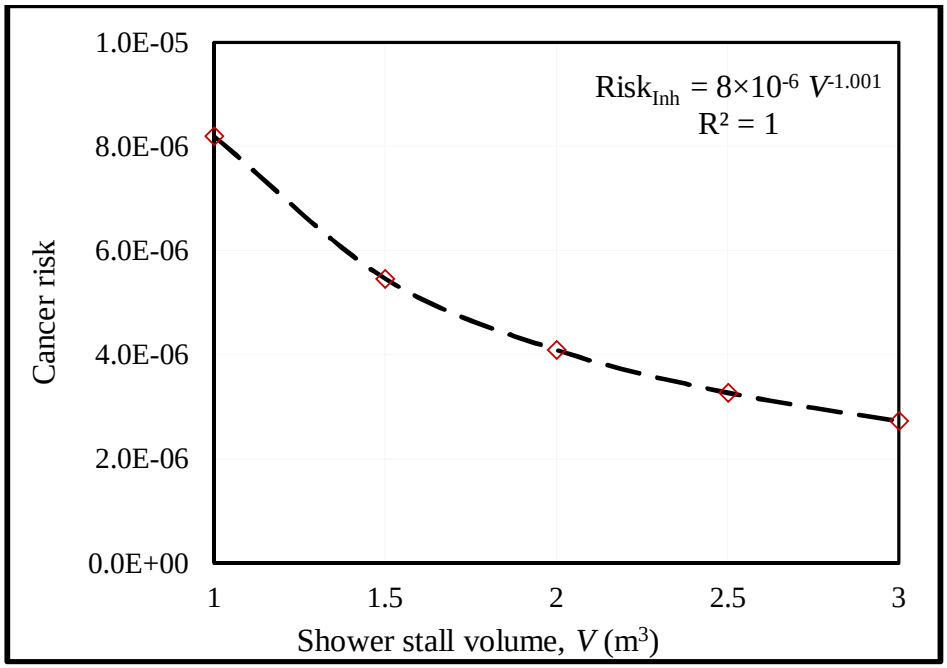


Figure 5.21: Effects of shower stall volume on cancer risk

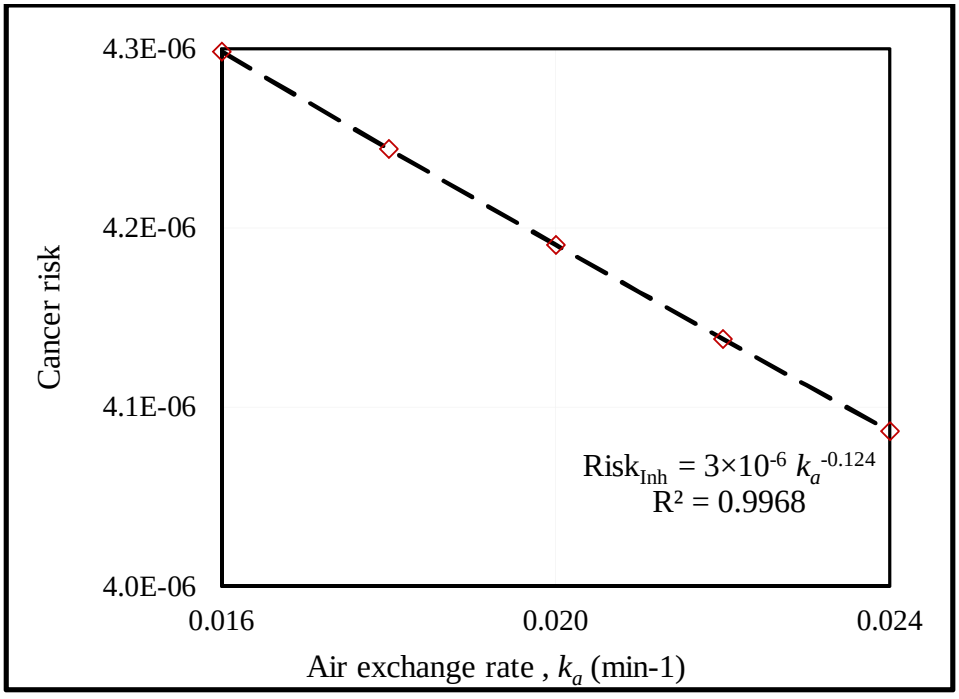


Figure 5.22: Effects of air exchange rate on cancer risk

From the above equations (Eq. 5.1-5.5), it can be seen that the risks through inhalation and dermal routes can be significantly controlled by increasing shower stall volume and air exchange rate and/or decreasing shower duration. However, increase in shower stall volume may need additional space, which is a function of space availability and municipal permit (where applicable). In addition, an increase in air exchange rate is often associated with power consumption, which can increase the power bills. There is a need to optimize these parameters to better control human exposure and risks.

5.4 Discussion

Desalination processes remove most of the organics from water resulting in lower level of NOM in desalinated water. The desalinated water is blended with the treated groundwater, rich in NOM, resulting in higher levels of NOM in the blended water. The groundwater in Saudi Arabia is typically polluted due to infiltration of untreated and treated domestic wastewater discharged in the sand dunes. Another possible source of contamination may be the leakage through the septic tanks. In addition, the aquifer properties might also be responsible for pollution to some extent. When treated groundwater is mixed with desalinated water, levels of NOM is likely to increase. This was reflected by the higher concentrations of DOC in blended water (average: 1.98 mg/L; range: 1.27 – 3.14 mg/L) than desalinated water (average: 0.78 mg/L; range: 0.39 – 1.68 mg/L).

Past study reported higher levels of bromide (up to 8000 µg/L) in groundwater in Saudi Arabia [223,224]. The bio-geo properties of the aquifers and possible intrusion of seawater from the Arabian Gulf and the Red Sea could have increased the levels of bromide in groundwater. This was also indicated by the lower concentrations of bromide in desalinated

water (average: 0.28 mg/L; range: 0.10 – 0.64 mg/L) than the blended water (average: 0.30 mg/L; range: 0.18 – 0.76 mg/L). Higher levels of NOM and bromide in the blended water resulted in higher concentrations of total and brominated THMs than the desalinated water. Presence of bromide ion in desalinated and blended water increases the fractions of brominated DBPs and reduces $CHCl_3$ in two pathways. Firstly, it produces HOBr, which is approximately 15 times more reactive than HOCl. Due to higher reactivity, the lighter chlorine atoms are substituted by the heavier bromine atoms resulting in increased brominated DBPs and decreased chlorinated DBPs. Secondly, HOBr is more reactive to hydrophilic fractions of NOM than that of HOCl resulting in additional formation of brominated DBPs. Generally, it is believed that desalinated seawater is safer than that of the freshwater sourced drinking water, due to the fact that most of the bromide and NOM are removed through desalination processes. However, the remaining levels of bromide (250 – 600 µg/L) and iodide (<4 – 16 µg/L) and addition of NOM through blending of treated groundwater provide an environment conducive to formation of higher levels of brominated and total DBPs. The brominated and iodinated DBPs are more toxic to human health than the chlorinated DBPs. There is a need to better understand DBPs occurrences and their risks to humans associated with desalinated and blended water.

For exposure and risk assessment, availability of data is important. In this study, DBPs data were also collected from several desalination plants and cities in Saudi Arabia. Using these data, statistical distributions were developed for THMs and 5000 random data were generated following Monte Carlo (MC) simulation. Application of MC simulation for THMs and other parameters has incorporated data variability and uncertainty to some extent. Using these data, lifetime excess cancer and non-cancer risks were estimated using

the slope factors and reference doses following the USEPA approaches. The slope factors represented the 95-percentile upper bound probability meaning that the predicted risks need to be interpreted accordingly. Further, slope factor was available for the oral route only, which was used for the other routes (e.g., dermal, inhalation) as well. This can be updated upon availability of new information in future. The variability in the toxicity data within the regulatory organizations (e.g., USEPA, OEHHA) needs further attention to better interpret the predicted risks. Using the predicted cancer risks, the DALY was estimated for different age groups. The overall DALY was estimated to be below the WHO guideline. The financial burden due to DALY was also estimated. However, the estimates represented only THMs while several other DBPs were also reported in desalinated and blended water. Estimation of cancer risks and DALY for all DBPs in desalinated and blended water is necessary to better evaluate human health risks.

Cancer risk can be controlled by reducing exposure during showering through increasing shower stall volume and air exchange rate and decreasing shower duration. The control of the early-life exposure can assist in reducing the lifetime risk significantly. For an example, 0 – <2 years of exposure contributed 25.4% cancer risk, which could be lower through reducing the early-life exposure. Moreover, concentration of bromide in desalinated and blended water need to be reduced to control brominated DBPs, which are more toxic to human health.

CHAPTER 6

CONCLUSIONS

In this study, occurrences of THMs in the desalinated and blended water were investigated for a period of 1 year (Feb 2014 – Jan 2015). The samples were collected and analyzed following the standard methods. THMs were found to be higher in the blended water than those in the desalinated water. The RO desalination plant effluents had higher levels of THMs and bromide than the thermal plants. In context to the Gulf countries, Saudi Arabian desalinated water had relatively lower concentrations of DBPs.

In the desalinated water, DBPs are formed in several stages (e.g., pre-treatment, storage and distribution networks within the desalination plants). Blending with treated groundwater typically increases the formation of DBPs, due mainly to higher levels of NOM in groundwater. The formation of DBPs continues through the water distribution pipes and plumbing systems. Following characterization of DBPs, this study presented the methodology to estimate human health risk and DALY from exposure to DBPs in desalinated and blended water. The database on THMs obtained in this study was expanded through incorporating the DBPs in the other desalination plants and water distribution networks from the major cities in Saudi Arabia. The data inclusion incorporated the data variability across the country, which has made the study more representative.

In this study, the risk assessment methodology was applied to investigate human exposure, risks and DALY in Saudi Arabia, which is the largest producer of desalinated water as a single country. The cancer risks of DBPs in desalinated and blended water were predicted

to be 1.78×10^{-5}, which exceeded the minimum risk level as recommended by the USEPA. Cancer risks through ingestion route were highest (65.4%) followed by dermal (23.5%) and inhalation (11.1%) routes. With respect to age groups, the highest contributor group was >16 years (45.3%), which had the largest lifespan (16+ to death). In contrast, the exposure during the early life (birth to < 2 years) contributed approximately 25.4% of the overall risks. Control of early life exposure can reduce the risk significantly. The cancer risks in terms of DALY was estimated to be 8.48×10^{-7} per person per year, which is below the reference risk level as recommended by the WHO. The DALY can be used for analyzing financial burden from cancer risks. It can also be used for cost-effectiveness analysis, which may help to improve the quality of desalinated water and may help to prioritize the hazardous material present in desalinated water.

This study has few limitations in context of data generation and data collection. The data generation requires the availability of standard chemicals on time, which was a challenge. Further, maintenance of equipment's upon sudden failure was another challenge. In addition, lack of expert technical staffs had some implications of the analytical schedule. Further, data were not available for all desalination plants across the country.

CHAPTER 7

RECOMMENDATIONS

Based on the findings of this study, the study proposes several scopes of future research. In this study, THMs were used for analysis and risk assessment, which were a fraction of various DBPs in desalinated water. Few other DBPs with possible cancer risks are HAAs, iodo-THMs, bromate, NDMA while sufficient information on these DBPs are not available to date to conduct risk analysis for desalinated and blended water. Future study may further look into these DBPs and their risks.

Data on DBPs were not available from all cities and plants. As such, the nationwide variability of DBPs, DBPs exposure and risks could not be predicted. In future, a database can be formulated for the entire country to better explain DBPs variability and exposure.

Although DBPs in supply water is a concern, no planned monitoring system is in place in the country. There is a need of better understanding the quality of desalinated and blended water.

Despite these limitations, this study sheds light on possible risks of DBPs in desalinated and blended water. Further, the coastal regions around the earth are the homes of approximately 2 billion populations. Many of these populations are exposed to water with relatively higher fractions brominated DBPs, which can be associated with elevated cancer risks. The coastal populations and the populations living on desalinated and blended water

may need a better understanding on the types of DBPs, their exposure and risks to protect public health.

Control of human exposure and risks can be attained through several approaches, including reducing the levels of DBPs in desalinated and blended water, which requires advanced treatments in different stages of desalinated water production (e.g., feed water to tap). As such, the additional cost is involved. At exposure level, risks can be significantly reduced by varying the shower stall volume, air exchange rate and through minimizing shower duration. In addition, past studies have demonstrated that the indoor handling, such as boiling, filtering through activated carbon filters and preserving water in a pitcher without lids might reduce THMs significantly. Future study may further look into optimization of these parameters in context to risk acceptance and cost.

Appendix

DBPs DATA FOR ANALYSIS

Concentration of THMs in µg/L in desalinated and blended water in Gulf countries

Location	Desalination Plant	DBPs	Range	Mean	SD	Median	Reference
Dhahran, Saudi Arabia		$CHCl_3$-WDS[2]	1.2-6.1	3.2	1.3		[38]
		BDCM-WDS	0.5-3.4	2	0.7		
		DBCM-WDS	0.0-1.2	0.5	0.3		
		$CHBr_3$-WDS	0.0-0.7	0.5	0.3		
Dhahran, Saudi Arabia		$CHCl_3$-WDS	1.264-9.3	5.51	2.18		[37]
		BDCM-WDS	0.53-1.31	0.8	0.18		
		DBCM-WDS	0.12-0.38	0.2	0.07		
		$CHBr_3$-WDS	0.1-0.24	0.12	0.03		
Red sea community, Saudi Arabia	Yanbu MSF/RO	$CHCl_3$-WDS	0.16-0.54	0.29			[173]
		BDCM-WDS	0.72-1.41	1.07			
		DBCM-WDS	1.21-2.33	1.83			
		$CHBr_3$-WDS	4.25-6.69	5.43			
Shuqaiq, Jazan, Saudi Arabia	Shuqaiq-1 MSF Plant	$CHCl_3$-DP[2]					[165]
		BDCM-DP		0.2			
		DBCM-DP		0.8			
		$CHBr_3$-DP		1.7			
Shuqaiq, Jazan, Saudi Arabia	Shuqaiq-2 MSF Plant	$CHCl_3$-DP					
		BDCM-DP		0.2			
		DBCM-DP		0.7			
		$CHBr_3$-DP		1.4			
Farasan Island, Jazan, Saudi Arabia	Farasan SWRO Plant	$CHCl_3$-DP					
		BDCM-DP		0.3			
		DBCM-DP		1.5			
		$CHBr_3$-DP		12.4			
Al-Birk, Makkah, Saudi Arabia	Al-Birk SWRO Plant	$CHCl_3$-DP					
		BDCM-DP		1.6			
		DBCM-DP		0.4			
		$CHBr_3$-DP		6.5			
Jubail	Al-jubail SWRO plant	$CHCl_3$-WDS	0.0-0.7	0.2			[174]
		BDCM-WDS	0.0-0.5	0.36			
		DBCM-WDS	0.0-1.0	0.86			
		$CHBr_3$-WDS	0.0-5.9	4.66			
Khobar	Al-Khobar MSF Plant	$CHCl_3$-WDS	0.0-0.05	0.02			
		BDCM-WDS	0.2-0.3	0.29			
		DBCM-WDS	0.9-1.1	0.99			
		$CHBr_3$-WDS	5.6-8.5	7.2			
Dammam		$CHCl_3$-WDS	0.0-0.04	0.02			
		BDCM-WDS	0.3-0.47	0.35			
		DBCM-WDS	1.0-1.9	1.4			
		$CHBr_3$-WDS	7.8-9.7	9.1			

Location	Desalination Plant	DBPs	Range	Mean	SD	Median	Reference
Qatif		$CHCl_3$-WDS	0.0-0.3	0.1			
		BDCM-WDS	0.20-0.28	0.25			
		DBCM-WDS	0.7-1.22	1.07			
		$CHBr_3$-WDS	7.7-9.7	8.54			
Rahima		$CHCl_3$-WDS					
		BDCM-WDS	0.25-0.3	0.29			
		DBCM-WDS	1.1-1.5	1.32			
		$CHBr_3$-WDS	9.0-12.0	10.67			
Khafji	Al-Khafji SWRO Plant	$CHCl_3$-WDS	0.0-0.9	0.45			
		BDCM-WDS	0.75-0.9	0.82			
		DBCM-WDS	0.86-0.92	0.9			
		$CHBr_3$-WDS	1.6-2.0	1.77			
Riyadh		$CHCl_3$-WDS	0.0-0.1	0.04			
		BDCM-WDS	0.34-0.5	0.42			
		DBCM-WDS	1.2-1.4	1.28			
		$CHBr_3$-WDS	2.3-2.7	2.42			
Dammam (Summer)	Dammam	TTHMs-WDS	0.22-26.86			9.1	[175]
Dammam (Winter)			0.12-28.85			18.17	
Riyadh (Summer)	Riyadh	TTHMs-WDS	0.95-8.37			5.58	
Riyadh (Winter)			1.32-8.05			4.9	
Buraydah (Summer)	Buraydah	TTHMs-WDS	0.51-5.00			0.83	
Buraydah (Winter)			0.78-3.90			1.02	
Hail (Summer)	Hail	TTHMs-WDS	1.10-2.54			1.43	
Hail (Winter)			1.14-6.30			1.41	
Madinah (Summer)	Madinah	TTHMs-WDS	5.37-11.00			4.57	
Madinah (Winter)			2.57-13.06			6.57	
Jeddah (Summer)	Jeddah	TTHMs-WDS	4.03-41.74			7.13	
Jeddah (Winter)			0.03-17.81			2.9	
Makkah (Summer)	Makkah	TTHMs-WDS	5.92-17.56			6.94	
Makkah (Winter)			1.39-19.29			3.17	
Abha (Summer)	Abha	TTHMs-WDS	1.43-1.88			1.52	
Abha (Winter)			1.12-1.31			1.25	
Jeddah, Saudi Arabia	Jeddah SWRO/MSF plant	$CHCl_3$-BW[2]	0.0-0.24	0.08			[154]
		CCl_4- BW	0-0.01	0.008			
		BDCM-BW	0-0.29	0.14			
		DBCM-BW	0.24-0.74	0.36			
		CHBr3-BW	3.85-29.38	8.92			
		TTHMs-BW	9.25-30.12	9.47			
Al-Jubail		$CHCl_3$-WDS		0.02			[176]
		BDCM-WDS		0.36			
		DBCM-WDS		0.76			
		$CHBr_3$-WDS		2.42			
Rahima		$CHCl_3$-WDS		0			
		BDCM-WDS		0.29			
		DBCM-WDS		1.32			
		$CHBr_3$-WDS		10.67			
Saudi Arabia	Red Sea Coast MSF plant	$CHCl_3$-TD[2]		ND			[17]
		BDCM-TD		0.15			
		DBCM-TD		0.12			
Dhahran, Saudi Arabia	Distilled seawater	TTHM	12.01-69.98				
Red Sea Coast, Saudi Arabia		TTHMs-TD		0.38			[20]
		TTHMs-ROP	0.36-66.7				

Location	Desalination Plant	DBPs	Range	Mean	SD	Median	Reference
		HAAs-ROP[2]	ND-0.71				
		HANs-TD		0.45			
		HANs-ROP	ND-1.98				
Jeddah, Saudi Arabia		TTHMs-TD	0.17-0.55				
		TTHMs-ROP	12.2-39.0				
Eastern Coast, SA		TTHMs-TD	0.09-3.48				
Al-jubail		HAAs-TD		1.6			
UMM Al Nar, UAE		TTHMs-WDS	7.0-15.0				
Kuwait		TTHMs-TD	2.7-22.8				
Kuwait		TTHMs		45.5	2.6		[169,208]
Al-Andalus	Doha Water Blending Complex	$CHCl_3$-WDS	0.0-1.96	0.52	0.68		
		BDCM-WDS	0.99-2.76	1.95	0.43		
		DBCM-WDS	2.74-7.18	4.61	1.05		
		$CHBr_3$-WDS	5.76-16.78	9.56	2.77		
Al-Jabriya, Kuwait	Doha Water Blending Complex	$CHCl_3$-WDS	0.0-2.91	0.9	0.98		
		BDCM-WDS	1.98-3.77	2.77	0.5		
		DBCM-WDS	7.0-13.73	9.19	1.5		
		$CHBr_3$-WDS	17.62-36.79	24.65	4.98		
Hawalli, Kuwait	Doha Water Blending Complex	$CHCl_3$-WDS	0.0-3.97	0.76	1.15		
		BDCM-WDS	1.27-3.78	2.22	0.57		
		DBCM-WDS	3.16-9.11	7.04	1.62		[172]
		$CHBr_3$-WDS	12.89-33.29	24.3	4.99		
Keifan, Kuwait	Shuwaikh Water Blending Complex	$CHCl_3$-WDS	0.0-3.11	0.92	1.07		
		BDCM-WDS	1.62-7.87	2.86	1.4		
		DBCM-WDS	2.75-9.11	5.6	1.41		
		$CHBr_3$-WDS	3.38-71.52	47.43	20.87		
Al-Sharq, Kuwait	Shuwaikh Water Blending Complex	$CHCl_3$-WDS	0.0-5.87	0.96	1.52		
		BDCM-WDS	1.61-3.34	2.4	0.49		
		DBCM-WDS	3.02-10.25	6.72	1.54		
		$CHBr_3$-WDS	7.41-77.42	44.51	20.34		
Qatar	Ras Laffan, Ras Abu-Fontas, Ras-Girtas desalination plant	$CHCl_3$-DP	0.01-4.96	0.6			
		BDCM-DP	0.01-2.66	0.21			
		DBCM-DP	0.01-2.74	0.52			
		$CHBr_3$-DP	3.99-72.95	20.89			
		$CHCl_3$-R[2]	0.01-4.55	0.8			
		BDCM-R	0.01-5.3	1.27			
		DBCM-R	0.01-2.21	0.89			[166]
		$CHBr_3$-R	1.65-72.97	15.11			
		$CHCl_3$-WDS	0.0-4.58	0.82			
		BDCM-WDS	0.01-26.24	2.59			
		DBCM-WDS	0.01-2.43	1.04			
		$CHBr_3$-WDS	1.44-55.97	14.6			
Muharaq, Bahrain		BDCM-WDS		0.57			
		DBCM-WDS		0.32	0.08		
		$CHBr_3$-WDS		2.88	0.16		
		TTHMs-WDS		3.77	0.16		
Hoora, Bahrain		BDCM-WDS		0.5			[177]
		DBCM-WDS		0.5	0.11		
		$CHBr_3$-WDS		0.28	0.06		
		TTHMs-WDS		1.28	0.11		
Salmania, Bahrain		BDCM-WDS		0.6	0.13		
		DBCM-WDS		0.73			

Location	Desalination Plant	DBPs	Range	Mean	SD	Median	Reference
		$CHBr_3$-WDS		2.3	0.3		
		TTHMs-WDS		3.63	0.3		
Mahooz, Bahrain		BDCM-WDS		1.2			
		DBCM-WDS		0.52	0.14		
		$CHBr_3$-WDS		0.86	0.12		
		TTHMs-WDS		2.58	0.14		
Musalla, Bahrain		BDCM-WDS					
		DBCM-WDS		0.64	0.05		
		$CHBr_3$-WDS		2.4	0.1		
		TTHMs-WDS		3.04	0.1		
Sanabis, Bahrain		BDCM-WDS					
		DBCM-WDS		0.73			
		$CHBr_3$-WDS		2.4	0.1		
		TTHMs-WDS		3.13	0.1		
Hammad Town, Bahrain		BDCM-WDS					
		DBCM-WDS					
		$CHBr_3$-WDS		2.9	0.1		
		TTHMs-WDS		2.9	0.1		
West Riffa, Bahrain		BDCM-WDS					
		DBCM-WDS		0.46			
		$CHBr_3$-WDS		5.9	0.15		
		TTHMs-WDS		6.4	0.16		
Sitra, Bahrain		BDCM-WDS		0.12	0.2		
		DBCM-WDS		0.87	0.03		
		$CHBr_3$-WDS		1.5	0.17		
		TTHMs-WDS		2.49	0.17		
Umm-al, Bahrain		BDCM-WDS					
		DBCM-WDS					
		$CHBr_3$-WDS		0.27	0.1		
		TTHMs-WDS		0.27	0.1		

WDS: Water distribution system; DP: Desalination plant; BW: Blended water; TD: Thermal distillate; ROP: RO permeate

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